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The Industrialization of Electrochemical Reactions

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The industrialization of electrochemical reactions

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The factors affecting the capital and running costs of electrochemical processes are reviewed and a design methodology based on the identification of design drivers is discussed. This methodology also highlights areas that require further research during the development phase of a process and so can be used as an aid to project management. Comparisons are made between electrochemical and chemical processes, it being shown that some electrochemical processes are already economically competitive, while others are likely to become so if further research is undertaken in areas identified by economic assessment rather than arbitrary choice.

Introduction

The literature on electrochemical synthesis stretches back nearly 150 years, yet relatively few reactions have been industrialized. Those that have been have been either virtually impossible to do any other way for thermodynamic reasons (e.g. aluminium smelting) or are relatively straightforward in their chemistry and offer simple separation and work up of anode and cathode products (e.g. chlor–alkali by mercury cell; it is interesting that the mercury cell is superior in the latter respects to the membrane cell which is replacing it owing to environmental pressures). In the main the successfully adopted processes are inorganic, although in principle in many cases electro-organic synthesis may offer an advantage over a conventional, catalytic route. For example an electrochemical step may: (i) be more selective than an equivalent chemical step (see table 1); (ii) permit elimination of one or more chemical steps (see figure 1); (iii) permit the use of an alternative feedstock (see figure 2); (iv) make commercially feasible the use of an expensive reagent (see figure 3); (v) replace a hazardous or socially unacceptable step with no loss in efficiency (see table 2); or (vi) be environmentally more benign (see table 3).

While there have been a number of conspicuous successes (Bott 1969; Nohe 1978; Baizer 1979; Danly 1979; Seko *et al.* 1979) in general electro-organic syntheses have not been scaled-up beyond the demonstration stage (Weinberg 1979) because cost projections were unpromising. However, in the last decade, progress in electrochemical engineering has been rapid, a number of useful texts have become available, and electrochemical reaction engineering has begun to emerge as a coherent discipline (Jansson 1980). It is now clear that many reactions have been studied at pilot scale in cells with inappropriate contacting patterns for chemical systems in which there are competing reaction pathways, which is the rule rather than the exception in organosynthesis. Further, optimization, however sophisticated, of an arbitrarily chosen initial design generally does not lead to lowest possible process cost; ideally the choice of the cell and its configuration should be variables in the optimization, which should encompass the whole plant, including preparation and separation steps. Clearly, without further constraint this is an enormous task (for example many experimental data would have to be produced across a very wide range, most of which would be irrelevant to later use), so it is helpful to devise a simple but

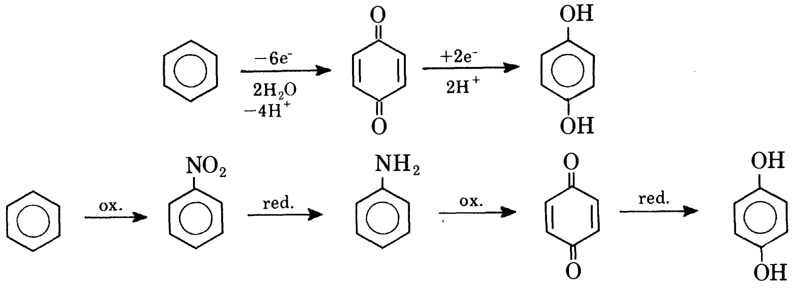


FIGURE 1. Elimination of steps: hydroquinone (Fremery *et al.* 1974).

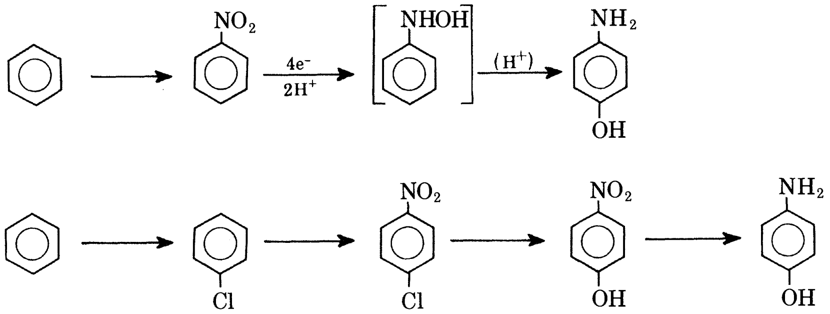


FIGURE 2. Alternative feedstock: synthesis of *p*-aminophenol (C. J. B. Developments Ltd 1973).

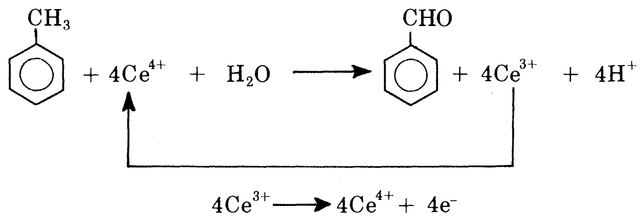


FIGURE 3. Regeneration of reagent: indirect oxidation of toluene (Kramer *et al.* 1980). Conditions: 1 M Ce, 5 M $HClO_4$, 1 : 15 toluene : hexane.

TABLE 1. MORE EFFICIENT (SELECTIVE) ELECTROCHEMICAL STEPS

			figures of merit†		
reaction	example	process	c.e.(%)	m.y.(%)	references
Kolbe	adipate→sebacate	Asahi	68	>80	Seko *et al.* (1979)
hydro-dimerization	acrylonitrile→adiponitrile	Monsanto Asahi	>85	>85	Baizer (1979), Danly (1979)
pinacolization	acetone→pinacol	Diamond	60	50–60	Shuster *et al.* (1976), Feoktistov & Lund (1973)
alkoxylation	furan→1,4-dihydro-dimethoxyfuran	B.A.S.F.	90	90	Nohe (1978)
reduction	α-methylindole→α-methyldihydroindole	Holliday	60	>90	van Tilborg (1978)
reduction	2-methoxynaphthalene→ ²Δene of ether (→β-tetralone)	Hoechst Pilot	>70	>90	Skaletz (1978)

† c.e., current efficiency; m.y., material yield.

Table 2. Replacement of hazardous or unacceptable reaction by electrochemical analogue (Nohe 1978)

reactant	product	chemical reagent
phthalic anhydride	dihydrophthalic acid	Na–Hg; no catalytic route
α-methylindole	α-methyl dihydroindole	Zn–Hg; waste disposal problem
anthranilic acid	*o*-aminobenzylalcohol	$LiAlH_4$; hazardous
acetone	pinacol	Mg–Hg; inefficient, disposal problem

Table 3. Environmental advantage

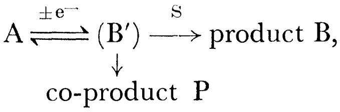
process	electrochemical	chemical	references
propylene, epoxidation	generation of hypohalide and base *in situ*	dump 2t/t of $CaCl_2$ or co-production of 3t/t of *t*-butanol	Simmrock (1978)
redox chemistry Cr^{VI}, Mn^{IV}, Ti^{III}, Ce^{IV}, Pd^0	small inventory of expensive reagent, regenerated continuously	high procurement costs; high dumping costs of spent reagent	van Tilborg (1978), Kramer *et al.* (1980)
halogenation	generation *in situ*; insensitive to legislation	bulk storage–transport; sensitive to legislation	
difficult reduction	no hazard	effluent problems (e.g. amalgams); hazardous or socially unacceptable ($Na–NH_3$, $NaNH_2$, $LiAlH_4$)	Nohe (1978)
oxidation, peroxidation	no hazard	hazardous or socially unacceptable (H_2O_2, CH_3CO_3H)	

quantitative method of selecting both the most promising system and most appropriate operating range before turning to full optimization. This can be done by identifying design drivers and allowing the design to evolve under their influence.

Design drivers

In the design of an independently operating system, such as a spacecraft, the principal design drivers – the two or three factors that dominate the design and to which all other factors are *shown* to be subordinate – are easily identifiable, and so the configuration evolves naturally and optimization is straightforward, even if it is not easy. Even though an electrochemical system may not be truly isolated (for example the electrochemical step may be one step in a long chain of steps), the same principle can be applied by costing the various subsystems of an assumed system design, identifying the design drivers and hence evolving better designs by iteration until the best candidate emerges, which can then be optimized. (The problem with optimizing *ab initio* is that the process will 'fine-tune' the first design, but will not necessarily drive towards a better design unless the routine is very sophisticated, which is unwarranted in early studies). It is important to recognize that the electrochemical *system* includes all the relevant unit processes as well as the cell and power supply. In fact, in pilot studies (Weinberg 1979)the individual subsystems have usually been costed, but long after the cell design has been frozen and the method of separation chosen, so that it has been of no help in system development. One merit of letting subsystem cost be the driving force is that it is not necessary to assume that any particular performance parameter, e.g. current efficiency or space time yield, has a particular significance; it may or may not in the light of the total cost obtained.

There is no space here to review the whole process, but the methodology can be illustrated by applying it to one subsystem, the electrochemical cell. Consider the generalized reaction



$$\begin{tikzcd} \mathrm{A} \arrow[r, shift left, "\pm e^-"] & (\mathrm{B}') \arrow[l, shift left] \arrow[r, "\mathrm{S}"] \arrow[d] & \text{product B,} \\ & \text{co-product P} & \end{tikzcd}$$

which is based on a reaction of commercial interest in which intermediate B′, produced in a fairly reversible electrochemical step, can either react with the substrate S to give the desired product B, or by one or more competing reactions (often of higher order) to form by-products, P. The loss reactions generally depend on the local concentration of B′ and hence on the current density, while parasitic gas evolution, decomposition of the solvent or electrochemical reaction of the substrate are usually small at low current densities (low overpotentials) but rise rapidly with current density (overpotential), so that the chemical–electrochemical performance may be as in table 4.

Table 4. Performance figures for model reaction

current density/(mA cm^{-2}) . . .	50	100	150	200
divided cell				
loss of B′ due to parallel reactions (%)	5.0	8.4	11.7	15.0
loss in c.e. due to gas evolution (%)	0.0	1.5	4.0	10.0
material yield (%)	95.0	92.6	88.3	85.0
overall current efficiency (%)	95.0	90.1	84.3	75.0
undivided cell				
loss of B′ due to parallel reaction and reversal electrochemical reaction (%)	7.5	12.6	17.6	22.5
loss in c.e. due to gas evolution (%)	0.0	1.5	4.0	10.0
material yield (%)	92.5	87.4	82.4	77.5
overall current efficiency (%)	92.5	85.9	78.4	67.5
annual electrode replacements	1	2	3	4
annual membrane replacements	1	2	3	4

For 1000 t/year (8000 h) of a chemical of relative molecular mass 120, the required production rate is 0.289 mol s^{-1}, corresponding to effective currents ((current density) × (total electrode area)) of 60.84–77.07 kA, depending on current efficiency and hence on current density.

A choice must now be made between the very many possible cell configurations (Jansson 1980); clearly there are too many to deal with them here in detail so, for the sake of illustration, consider three variations of a plate and frame (filterpress) design†; a fairly conventional design with graphite electrodes 1.2 m × 0.5 m (effective area 1.0 m × 0.5 m), an ion exchange membrane and a 3 mm electrode–membrane spacing,‡ a divided cell with more complex frames so that the electrode–membrane spacing could be reduced to 1 mm; and an undivided cell with a novel electrode (McMackins 1980) so that the electrode–electrode spacing could be reduced to 1 mm while retaining frames of sensible thickness. Provided that the mechanical design of the cell is reasonably detailed, the approximate capital costs can readily be established by well known principles (Keating & Sutlić 1979; Danly 1979*b*, 1980) and are shown in outline

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† In the real case, other designs had already been eliminated by the same process.

‡ Dimensions are not necessarily optimal but are determined by stock sizes of graphite plates, ion exchange membranes and polypropylene sheet.

in table 5 for the first design. It has been assumed that the resistivity of the solution is 85 Ω cm (a typical value for a non-aqueous system), the resistance of the membrane is 25 Ω and that the cells are grouped in banks requiring approximately 650 V d.c., since transformer–rectifiers have a shallow cost minimum at about this point. With such a high solution-phase resistance current, bypassing would be negligible (Danly & Burnett 1979) and has been ignored here for the sake of simplicity and generality. For similar reasons the lifetimes of electrodes and membranes are assumed to be linearly proportional to current density (table 4); the capital costs per unit electrode area obtained are of the same magnitude as those obtained by Keating & Sutlić when adjusted to 1980 prices.

TABLE 5. SUMMARY OF CAPITAL COSTS (THOUSANDS OF DOLLARS) FOR DESIGN 1

current density/(mA cm^{-2}) . . .	50	100	150	200
electrodes, etc. at \$125.95	31.24	16.63	11.84	10.08
gaskets, etc. at \$6.46	3.15	1.68	1.19	1.01
membrane assemblies at \$232.87	56.82	30.27	21.42	18.16
mechanical structure and presses†	87.16	46.42	32.86	27.86
	178.37	**95.00**	**67.31**	**57.11**
ancillaries (15%)	26.86	14.25	10.10	8.57
	205.13	**109.25**	**77.41**	**65.88**
installed cell capital (× 5)	1025.65	546.25	387.05	328.40
installed rectifiers, etc. (× 5)	45.12	79.56	117.81	171.06
total installed capital (cells and electrical gear)	**1070.77**	**625.81**	**504.86**	**499.46**
	8800	9755	11047	12963 \$m^{-2}
	818	906	1026	1200 \$ft^{-2}

† based on \$25000 for 35 m^2 of electrode area (Danly 1980).

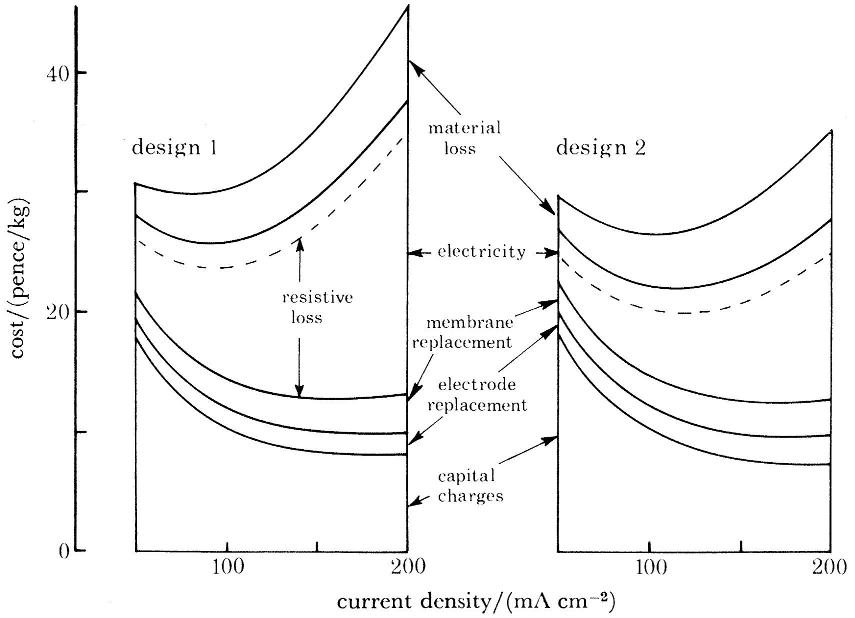

FIGURE 4. Identification of design drivers.

If it is assumed that the required rate of return on investment is 15%, with another 15% for taxes and other charges and 10% for depreciation, then the capital charge per kilogram of product can be established, and this is shown in figure 4 with charges for electrode and membrane replacement, loss of feedstock (at 50 p/kg) and electricity (2.3 p/kWh). Clearly for design 1 (3 mm semi-gap), the two most important items are capital charges and electricity, particularly the latter since a very high proportion of it (broken line) is lost in resistive heating, which imposes a further capital burden on the system by the need to provide heat exchangers to remove up to 1.2 MW of heat, together with an additional running cost for cooling water (note, even at this stage, the interaction with other items of plant). For design 1, cooling costs are more important even than membrane or electrode replacement, so that energy loss is the design driver.

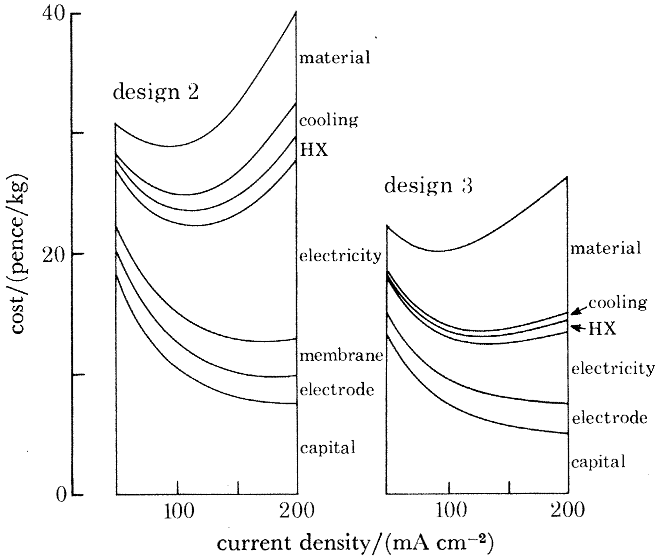

Figure 5. Design drivers: divided and undivided cells.

A redesign of the electrodes, flow-channels and membrane assembly to reduce the electrode–membrane gap to 1 mm produces a significant saving in energy for a small increase in capital charges due to marginally higher fabrication costs of the more complicated structure (design 2, figure 4). Since the chemical performance was assumed to be independent of the gap, the downstream separation costs associated with designs 1 and 2 would be the same, and therefore design 2 would be preferred. An even larger saving in energy can be obtained on going to an undivided cell (design 3, figure 5) so that even the heat exchanger and cooling water costs become insignificant. An additional advantage is that, although the electrodes and frames are more expensive, the elimination of the membrane actually lowers the overall capital cost. The penalty, of course, is that the selectivity in the undivided cell is worse (table 4) so the loss of material is greater in design 3 than design 2. Nevertheless, in many processes that have been piloted and rejected it may be economically advantageous to accept a lower selectivity for the sake of a lower capital cost system; the question hinges on the nature of the competing reactions. If the loss reaction is, say, an oxidation of the starting material to CO_2 and a hydrocarbon little additional penalty is incurred beyond the loss of material and electrictiy, already included in the assessment; however, if the loss reaction leads, say, to oligomers that are hard to separate, the consequential cost may be large and prohibitive. In the present example, if the incremental cost of dealing with the additional by-products exceeds about 9 p/kg, then design 2 may still be preferred.

Of course, in a specific case, separation and other costs can be added to the overall assessment in the first place to establish the design drivers for the electrochemical system as a whole. When repeated for a variety of cells and a number of methods of separation, the system most likely to be best emerges quite naturally. Sometimes rather unexpected results are obtained at this stage that change the direction of the supporting research programme, so the technique is also of help in project management. For example, in the above case, whatever the assumption the cost minimum was never far away from 100 mA cm^{-2}, so graphite would be a realistic choice of electrode material and work arbitrarily directed towards obtaining higher current densities (often an academic goal) would be wasted. Conversely, had a current density of 300 mA cm^{-3} been indicated, then the initial assumptions would have been invalid and a different choice of material would have been necessary. (Even at low current density a different material might be preferable on the grounds of increased lifetime, but the economic desirability of this would be immediately testable by the same method.)

Processing costs

The costs of distillation, solvent extraction, etc., of a product from a known mixture can readily be established by conventional techniques of chemical engineering (Peters & Timmerhaus 1968; Backhurst & Harker 1973,) as they can for a catalytic process, but one must note that certain additional processing costs may be introduced by virtue of the process's being electrochemical, in particular the recovery of electrolyte. In the Monsanto process (Danly 1973, 1979*a*), for example, the adiponitrile product is extracted from a slipstream with acrylonitrile, and the quaternary ammonium salt (QAS) electrolyte is then extracted from this solvent with

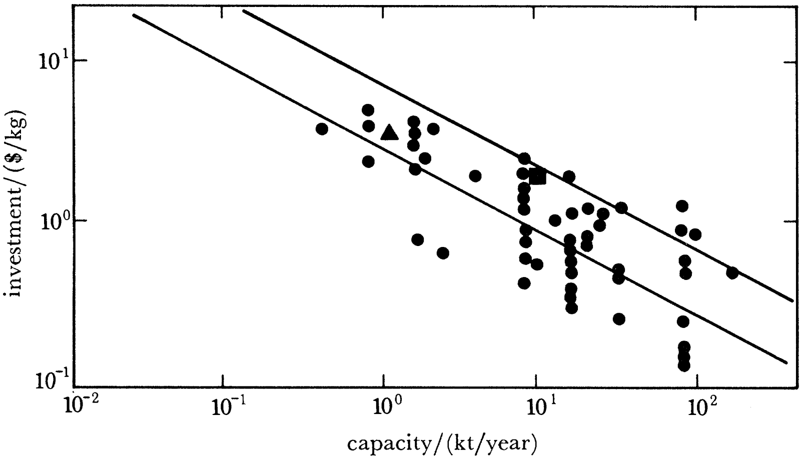

FIGURE 6. Comparison of investment costs of catalytic and electrochemical processes: ●, chemical process (acetic acid, acetone, butanol, styrene, acetylene, phthalic anhydride, acrylonitrile, ethanol, ethylene oxide, polyvinyl chloride, ethylene glycol, isoprene, oxo-alcohols, polyethylene, polypropylene formaldehyde); ▲, benzaldehyde; ■, hydroquinone. The area between the parallel lines indicates electro-organic process. Relative molecular mass 100; c.e. 70%; m.y. 70%, two electrons. (After Fitzjohn (1975).)

water; after concentration by evaporation the QAS is returned to the cells, so that the inventory of QAS is conserved, but recovery costs are incurred. Also it is sometimes necessary to prepare the feed in a special form, as in the Asahi process (Seko *et al.* 1979) for the manufacture of sebacic acid from adipic acid by the Crum–Brown–Walker reaction, where the electrolysis loop represents a small fraction of the total plant. Although in both of these cases the overall process is still economical, clearly considerable attention must be paid to minimizing such additional costs.

While no detailed process costs are generally available for either the Monsanto or the Asahi process, estimates are available for the production of hydroquinone from benzene (Fremery *et al.* 1974; Danly 1980), and for the oxidation of toluene to benzaldehyde (Kramer *et al.* 1980), which will serve as guides. The first reaction is sketched in figure 1 and the second in figure 3. In the U.R.B.K. process (Fremery *et al.* 1974), benzene is oxidized to quinone in the anode compartment of a divided cell and then (after a slight change in condition) is reduced to hydroquinone in the cathode compartment; despite the lack of charge balance it is therefore a case of a paired reaction. In contrast the E.T.H. process (Kramer *et al.* 1980) is an indirect oxidation, the electrochemical part being the regeneration of the redox reagent Ce^{IV}, interestingly with simultaneous extraction of the product into *n*-hexane to obtain a high selectivity. The capital costs and process costs in each case have been cast in the same form and are shown in tables 6 and 7. Despite the differences in chemistry and work-up procedures, the pattern of capital expenditure is rather similar; cell costs and process equipment costs are large and comparable while other costs are relatively small. Likewise, raw materials, utilities and capital-

TABLE 6. INSTALLED CAPITAL COSTS FOR HYDROQUINONE AND BENZALDEHYDE PROCESSES

	hydroquinone		benzaldehyde	
	(k$)	(%)	(kSfr)	(%)
cell + electrodes	8964	46	2145†	37
rectifier, etc.	2775	14	596†	10
process equipment	7220	37	2673†	46
building	660	3	414	7
totals	**19619**	**100**	**5828**	**100**

† Ancillary and installation costs spread proportionately between the three main headings.

TABLE 7. PROCESS COSTS FOR HYDROQUINONE AND BENZALDEHYDE PROCESSES

	hydroquinone		benzaldehyde	
	(c/kg)	(%)	(c/kg)	(%)
raw materials	12.64	19	4.50	12
utilities	14.59	22	7.25	20
maintenance	2.25	3	3.46	9
labour	2.53	4	4.44	12
overheads	5.38	8	1.33	4
admin., sales and research	6.66	10	4.42	12
depreciation	6.46	10	7.73	21
return on investment	16.12†	24	3.71‡	10
totals	**66.63**	**100**	**36.84**	**100**
current market price	*ca.* 77		*ca.* 54	

†, 25 % on capital; ‡, 8 % interest on capital.

related charges are major process costs, as they were in the hypothetical case discussed earlier. By using tables 6 and 7 as models, the order of magnitudes of process costs can be projected from cell capital if better data are not to hand. The very high cost of process equipment underlines the desirability of considering separation at a very early stage of a project, i.e. establishing whether or not it is the design driver, which it well may be. It also emphasizes the need, in most cases, to ensure high selectivity of reaction.

Selectivity

Despite its importance, relatively little has been published on the influence of engineering variables on selectivity. In general, if the follow-up reactions to an electron transfer are very fast or very slow, engineering design is not very crucial (Johnson 1981); in the first case the reaction takes place in the diffuse layer, which is insensitive to external conditions because of the different scale lengths involved (Jansson 1980), and in the second reaction takes place anywhere in the system, which thus approximates a stirred tank. However, a surprising number of systems are sensitive to mixing, owing either to a dependence on local concentration (Tomov 1978; Tomov & Jansson 1980; Johnson 1981; Johnson & Jansson 1980; Plzak *et al.* 1974) or to the extreme conditions, e.g. pH, which can occur in a reaction layer close to the electrode (Tomov 1978; Jansson & Tomov 1978; Marshall 1981; Baizer 1979). As it is now possible to measure the reaction environment in various cells by physical means (Fleischmann & Justinjanović 1980; Ferreira 1979; Fleischmann & Jansson 1975; Marshall 1981; Sarfarazi 1979), it is also possible to some extent to tailor the reaction environment to the needs of the desired reaction (Jansson & Fleischmann 1979; Jansson & Johnson 1981; Jansson & Tomov 1978). Further, some electrochemical cells offer unique contacting patterns so that a coupled sequence of reactions can be driven in a desired direction, as in the indirect epoxidation of propylene in a trickle bed (Bousoulengas *et al.* 1979; Ellis & Jansson 1980, 1981), which takes place with very high selectivity.

In three-dimensional electrodes the non-uniform current–potential distribution adds a complicating factor, since the driving force for the electrochemical reaction varies with position (Newman & Tiedemann 1978) and there may be zones of a monopolar bed, for example, where the potential is high enough to drive another reaction such as reduction of nitrobenzene to aniline instead of *p*-aminophenol (Hamilton & Goodridge 1980; C. J. B. Developments 1973). There are many sophisticated models of three-dimensional electrodes (Newman & Tiedemann 1978; Fleischmann & Ibrisagić 1980) that can be used to 'fine-tune' design, but in the preliminary assessment approximate models based on analogies with electrical delay lines (McKubre & MacDonald 1981) and chemical reaction engineering (Fleischmann & Jansson 1980*a*, *b*) are more convenient. In general, the development of a suite of approximate models with fast algorithms for all kinds of electrochemical reactors would be very helpful in process design.

Very much more work needs to be done in the area of selectivity in electrochemical reactors because of the leverage that selectivity has on the costs of the complete electrochemical process.

Conclusion

While much more work needs to be done in the development of electrochemical engineering, so that the potential for advance is great, a rational design methodology does exist for both the rapid assessment of potentially attractive electrochemical processes and for the optimization of selected systems (Goodridge 1980; Plimley 1981). In fact, many electrochemical routes are already competitive with catalytic ones. For example, figure 6 is based on a comparison by Fitzjohn (1975) of a hypothetical electro-organic process with a number of well established chemical processes. Also shown on figure 6 are approximate values for the hydroquinone and benzaldehyde processes discussed above; even without taking 5 years' inflation into account it can be seen that in terms of capital cost they are competitive. Since 1975 there has been considerable progress in electrochemical engineering design so that the electrochemical costs are now probably rather high compared with the costs of the catalytic processes. (Note that in figure 6 the current efficiency and material yield are each assumed only to be 70%.) Of course, the viability of any given process must be established by cost, but there is reason to expect that in many cases an electrochemical reaction may be the method of choice, and any company that arbitrarily dismisses electrochemistry from consideration relinquishes a potentially powerful process technology on the basis of nothing more than prejudice, which, however justified in the past, is certainly not justified now.

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