# Electrosynthesis: Speculations on Industrial Electrochemistry [and Discussion]

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*Phil. Trans. R. Soc. Lond. A* 1981 **302**, 247-252
doi: 10.1098/rsta.1981.0164

*Phil. Trans. R. Soc. Lond.* A **302,** 247–252 (1981)
*Printed in Great Britain*

# ELECTROSYNTHESIS
## Speculations on industrial electrochemistry

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Large-scale electrochemical processes are commonly used where ionic raw materials are converted into finished products that are either metals or covalently bound. Examples are aluminium production and the chlor-alkali industry. In a few cases they are used to carry out chemically difficult processes such as acrylonitrile dimerization.

The advances in electrochemistry and the related electrochemical engineering, coupled with sharply increased energy costs, have led to a new appraisal of electrochemistry in the chemical process industries. It seems likely that the novel electrochemical routes will emerge in situations where the special advantages of electrochemistry such as energy specificity, absence of toxic and reactive intermediates, chemical selectivity, and specific activation of small molecules can be applied. Examples of this will possibly come in the production of chlorine chemicals, nitrogen chemicals, use of CO and $CO_2$ as carbon sources, and in selective oxidation processes that permit combined production of chemical intermediates and electrical energy.

### INTRODUCTION

Industrial chemistry must always be concerned with the efficient use of resources in the production of chemicals that meet the needs of society. As seen from the perspective of 1980, the two most critical resources are seen to be energy and capital to build the next generation of plant. The effective use of these two, alongside the constraints that chemical plant must be safe and environmentally acceptable, provides the background against which electrochemical technology for the future must be judged.

The large-scale use of electrochemical technology today is dominated by extractive metallurgy or metal refining. In the heartland of the chemical industry, electrochemical processes are the exception rather than the rule. Of the chemical intermediates made in large quantities, only adiponitrile is made by an electrochemical route. The really large-scale use is confined to the production of chlorine, caustic soda and hydrogen from sodium chloride solution. This process is ideally suited to electrochemistry, as the feedstock is an ionic solution and there is a market for the products produced at each electrode, effectively using each faraday twice.

Some barriers to the further use of electrochemical technology in chemical synthesis are effectively illustrated by a recent report by the Electrochemical Technology Corporation (1979). This report surveyed the production of 220 organic chemicals produced on a scale of 10000 t/year or greater in the U.S.A. Electro-organic synthetic routes to 95 of these were identified in a literature search. Nine were studied in more detail and two were identified, adiponitrile and methyl ethyl ketone, where the electrochemical process gave a more energy-efficient route. This rather meagre yield is not too surprising given the method used. If energy efficient processes that were not too expensive in plant capital were available, they would already be in use. If electrochemical processes are to play a more important role in the future, and we believe that they will, then some creative thinking is needed by the chemical industry in setting challenging yet realistic targets. This will provide an indication of the scientific and technological advances that are needed and which the industry and their colleagues in academic institutions can jointly seek.

As a justification for the speculative suggestions that we are about to make, we quote from Sir Philip Sidney (1554–1586), a noted Elizabethan who played an important role in the foundation of Jesus College, Oxford, where one of us studied: 'Who shoots at the mid-day sun, though he be sure he shall never hit the mark; yet as sure he is he shall shoot higher than who aims but at a bush' (*Arcadia*).

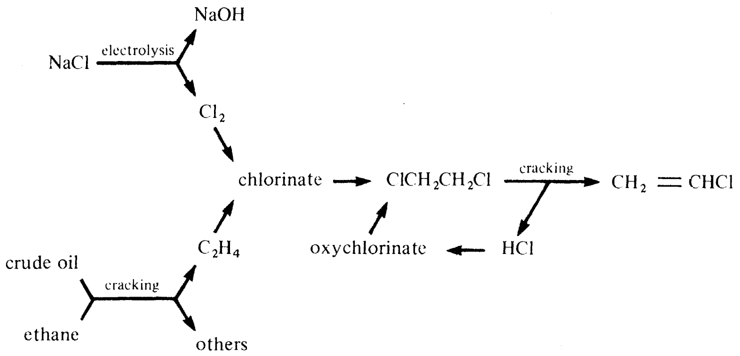

FIGURE 1

## TARGETS FOR INDUSTRIAL ELECTROCHEMISTRY

In choosing the target areas to which we will refer, we have selected areas of chemical technology where there is already substantial production and where economies in energy and capital costs are highly desirable. Additionally we have tried to indicate a path that, although difficult, does appear to exist.

Three target areas are considered, but many others are possible.

1. *Avoidance of energy switchbacks.* Chemical technology often involves sequential reactions in which a primary feedstock is raised to a high energy; this energy is then used to drive a further sequence of reactions. In some cases this process is repeated several times. Both energy and capital can be saved if direct routes, which could be electrochemical, could be devised. This can be illustrated by two examples, one the production of chlorine compounds, notably vinyl chloride, and the other the production of aromatic amines, for example aniline.

2. *Coupling of oxidative and reductive reactions.* In most electro-organic synthetic reactions now used, only one electrode reaction is useful. Chlor-alkali production is the major exception. This illustrates that where energy costs are important it is worth the trouble involved in the stoichiometric linking of two products that serve different end users, to make energy savings.

3. *Use of air cathodes coupled to electrochemical oxidation.* In most electro-organic oxidations, the cathode reaction involves the evolution of hydrogen. Recovery of energy from this hydrogen by reaction with oxygen at the electrode will nearly always provide enough energy to drive the desired reaction and in some cases could provide significant quantities of d.c. power, which could be used to drive other electrochemical reactions.

### *Avoidance of energy switchbacks*

The most widely used reaction sequence for the production of vinyl chloride is shown in figure 1. Energy is used in the electrolysis of brine and in the gas-phase thermal decomposition of 1,2-dichloroethane to give vinyl chloride. Energy is effectively lost in the chlorination of ethylene, where cooling water is used to control the reaction temperature. Some energy is recovered in the oxychlorination step, which is exothermic and carried out at about 250° C. The overall effect is that much more energy is used per tonne of vinyl chloride than the theoretical requirement for the overall reaction

$$NaCl + C_2H_4 + H_2O \rightarrow CH_2{=}CHCl + NaOH + H_2.$$

It has long been known that some of this energy could be saved by using air cathodes in the chlor-alkali cell, and much work has been done on this. It is now likely that operable schemes will be developed. Other approaches are possible.

TABLE 1. ENERGY RECOVERY IN NITRIC ACID PRODUCTION

$$NH_3 \xrightarrow{O_2} NO \xrightarrow[H_2O]{O_2} HNO_3 \quad \Delta G = 271\ \mathrm{kJ/mol}$$

High-temperature solid electrolyte fuel cell

$NH_3$, NO, $N_2$, Pt–$ZrO_2$ (8 % $Y_2O_3$)–Pt, air

$$2NH_3 + 5O^{2-} \longrightarrow 2NO + 3H_2O + 10e^- \quad \text{o.c.v.} = 1.1\ \mathrm{V}$$

(R. Farr & C. Vayenas 1980)

Another example is the use of copper chloride as a chlorine carrier with the reaction sequence

$$2CuCl_2 + C_2H_4 \rightarrow ClCH_2CH_2Cl + 2CuCl,$$

$$2CuCl + 2Cl^- \rightarrow 2CuCl_2 + 2e^-,$$

thus replacing the discharge of $Cl^-$ with the oxidation of $Cu^+$ as the anode process. These basic reactions are known (Spector *et al.* 1967), and we ourselves have shown that the combination of these steps with alkali production is possible. There is no reason in principle why a suitable reagent for the conversion of ethylene to vinyl chloride should not exist: the formally analogous production of vinyl acetate is carried out. However, the relative nucleophilicity of acetate and chloride makes the chloride case more difficult and no system is as yet known.

Similar in principle is the production of nitric acid from ammonia (table 1). Vayenas and his coworkers at the Massachusetts Institute of Technology have shown (Vayenas & Farr 1980) that it is possible to devise an electrochemical cell using a stabilized zirconia separator which can produce electricity from the oxidation of ammonia to nitric oxide. The current density so far achieved is low but the developing technology of zirconia fabrication does hold out promise of improvement. A more general research target would be a better oxide ion conductor than $ZrO_2$.

The subsequent use of nitric acid to form nitrobenzene, which is then used to produce aniline, is a further example of an energy switchback that could possibly be simplified by electrocatalytic routes.

### *Coupling of oxidative and reductive reactions*

The concept of coupling oxidative and reductive reactions is not scientifically innovative in itself, but it does call for imagination in terms of choosing appropriate pairs and in the cell separation, and possibly the reaction pathways.

A very speculative example is the coproduction of aluminium, chlorine and alkali. Here it is possible to conceive a three-compartment cell in which the anode compartment contains salt and the cathode compartment contains alumina; the centre compartment is confined by two separators: on the anode side a sodium ion conductor and on the cathode side an oxide ion conductor. The passage of one faraday would then liberate one gram atom of chlorine at the anode, one-third of a gram atom of aluminium at the cathode, and transfer one mole of $Na_2O$ into the centre compartment. By comparison with existing technology, the liberation of useful aluminium replaces the less useful hydrogen and chlorine replaces oxygen. Thus aluminium and chlorine are coproduced for the same faraday, instead of using two.

Coming to much less speculative examples, the addition of cyanide ion to butadine is an oxidative process:

$$CH_2{=}CH{-}CH{=}CH_2 + 2CN^- \rightarrow CN.CH_2{-}CH{=}CH.CH_2CN + 2e^-,$$

which could be coupled to the reduction

$$CN.CH_2CH{=}CH.CH_2.CN + 5H_2 \rightarrow NH_2(CH_2)_6NH_2$$

for at least part of the reduction required.

The reduction of nitrobenzene to aniline could be coupled to an electrochemical oxidation. A possible partner required on a corresponding scale is the production of methyl methacrylate from isobutene, a process now involving heterogeneous catalysis with about a 60% overall yield. The production of 4,4′-bipyridyl from pyridine involves reductive coupling followed by oxidation. The present process uses sodium metal and oxygen, involving separation of sodium oxygen compounds from the product stream. Many more examples could be given.

### *Use of air cathodes coupled to electrochemical oxidation*

This is similar in concept to the last section and to the work by Vyenas on ammonia oxidation. Most oxidative electrochemical reactions split water, so that an oxidative reaction is coupled with hydrogen evolution. The electrochemical oxidation of this hydrogen provides the energy to drive the redox couple used on the oxidative part of this cycle.

A very elegant example of how this can be done is given by Murray and Meyer and their coworkers at University of North Carolina (Meyer *et al.* 1980). They use a ruthenium complex system which is a stable $Ru^{II}$–$Ru^{IV}$ couple with a reversible e.m.f. of 0.7 V (against saturated calomel electrode) to drive oxidative processes in very high yield. At the half-cell voltage required by the oxidation, hydrogen oxidation at the cathode would yield surplus power. In some ways this may be more attractive for stationary power generation than a total combustion fuel cell, as the cell has two outputs, useful chemicals and power.

Some progress in this direction is being made by electrocatalytic reactions with the use of chemically modified electrodes. For example, at carbon electrodes with (tetrakis (*p*-aminophenyl) porphyrin) iron, (protoporphyrin IX) iron, (tetrasulphonatophthalocyanine) cobalt, and (tetrapyridylporphyrin) cobalt, and at platinum electrodes poly(*p*-nitrostyrene). These all help to achieve rapid reduction to the hydroxide ion (see, for example, Snell & Keenan 1980).

## Requirement for new science

The prediction of really new effects is rarely successful; the only prediction we will make is that by 1990 at least one major advance will be made that none of us has now thought of. However, it is possible to see advancing lines of research that seem likely to make some of the targets referred to above attainable.

First, much work is being devoted to the activation of small molecules such as nitrogen and carbon monoxide. This is often related to the interaction of these compounds with transition metals and their complexes. This will open up possibilities for elegant electrochemical processes that use electrodes to bias the reactivity or to drive the necessary redox couples. In particular, the growing body of work on chemically modified electrodes for electrocatalytic reactions will be a fertile field for new electrochemical technology.

Secondly, as one tries to combine anodic and cathodic processes into one cell system, it becomes more and more important to have a cell separator that can pass selected ions only as the current carriers between the two half-cell reactions. The emergence of the Nafion, Flemion and other membrane systems for chlor-alkali production already points to this as a practical proposition; Raipore is similarly significant as an anionic membrane. As membrane separations become more sophisticated, for example distinguishing between two positive ions, so the membrane itself will need to be carefully designed for the application. Biological membranes already do this, although at low rates and only in carefully controlled environments.

The electrochemical regeneration of inorganic couples that are themselves reaction catalysts is well known. It will continue to be important. The extension of this principle to chemically modified electrodes will make this even more significant. As the chemical reaction then takes place on the electrode surface or in its immediate boundary layer, this also means that the reaction environment can be substantially different from the homogeneous solution in the cell. This offers a further control parameter that can be adjusted to gain selectivity.

The need for high current densities to keep down capital costs, and the relation between cell resistance and electrolyte conductivity, make it desirable that aqueous systems be used as current carriers. By contrast, solubility relations and often reactivity patterns demand that the desired chemical reaction take place in an organic solvent. The development of two-phase electrolysis is highly significant in this context.

Electrochemistry is, after all, chemistry. It will benefit from the continuing development of chemical science. Electrochemical engineering is similarly a branch of engineering. Both have their special features which can help them make a more significant contribution to a less energetic future.

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## *Discussion*

G. T. Rogers (*Materials Development Division, A.E.R.E. Harwell, U.K.*). This paper makes the point that not only are energy costs expected to continue to rise but also that in the recent past the cost of capital has been increasing faster than inflation. These two factors have somewhat opposite influences on the development of electrochemical processes. When energy costs predominate, the emphasis will be on reducing overpotentials and ohmic losses by various means but generally by reducing current densities at the expense of larger and therefore more costly electrolytic cells. If the cost of capital is predominant, the reverse applies: there will be a premium on high current density processes.

Would Dr Roberts be prepared to speculate on how he thinks the relative costs of energy and capital may change within the timescale covered by his paper?

H. L. Roberts. Within the timescale covered by my paper, both capital and energy costs will rise. If I have to guess it is that capital costs will outpace non-oil dependent energy. The essential point that we were making was that electrochemical research should avoid the trade-off area between capital cost and energy saving, as net gains are likely to be quite small. The objective should be to look for areas where an electrochemical process can eliminate reaction steps involving energy switchbacks. In this way both capital and energy savings can be made, as illustrated in the paper for vinyl chloride.