

NEWS

Book reviews**Electrosynthesis: from laboratory, to pilot, to production**

Edited by J. D. Genders and D. Pletcher

The Electrosynthesis Company Inc., 1990, pp. 242, £25.00.

The 15 chapters, written by 15 sets of authors, making up this volume, resulting from the third International Forum on Electrolysis in the Chemical Industry held in Fort Lauderdale, Florida, is a collection of courses, lectures and case studies. The bias is towards organic electrosynthesis, nine chapters, with three, rather short, chapters dealing with examples of inorganic electrosynthesis. The three introductory chapters occupy approximately 35% of the text and constitute the course elements from the forum covering fundamental aspects of electrochemical technology and engineering. The publication is 35% of good quality and, unlike many other collections of meeting or symposia papers, is printed in consistent typescript.

Chapter 1 provides an introduction by reviewing electrochemical processes at their current status. It gives a now familiar tabular presentation of commercial and pilot scale electro-organic processes, the major focus of the chapter and considers their scope and future. Inorganic chemical processes are briefly mentioned.

Chapter 2 give a comprehensive account of electrosynthesis. It broaches factors which affect the commercial success of electrochemical processes, provides some basic principles of electrochemical kinetics, aspects of mass transport, engineering design parameters, cell design and 'scale up'.

Chapter 3 provides a practical guide to the choice of electrode materials, separators and cell designs. Solid background is provided to the structure, properties, mode of operation and applications of ion-exchange membrane. General purpose flow electrolyzers commercially available are discussed.

Chapter 4 is the first of many descriptions of electrochemical technology in synthesis and describes experiences of the authors in the development of two industrial electrochemical processes; one direct and one indirect. The indirect process uses Cr (VI) generated by anodic oxidation in acid sulphate to produce anthraquinone from anthracene. Aspects of the upgrading of tank electrolyzers to flow cells are discussed which included the introduction of Nafion cation-exchange membranes. The direct process was the cathodic reduction of a substituted indole to an indolene (2 methyl) on lead. A highlighted feature is the common loss in efficiency of the reaction due to contamination of the cathode arising from impurities in the sulphuric acid feedstock. A common feature of both example syntheses is that the processes deal with a solid reactant phase.

This first hand account of industrial type process

developments gives some "interesting tips" for would-be practitioners, or perhaps non process engineers, eg always look for simplifications and improvements, train your plant operators, use flow indicators and monitors!

Chapter 5 gives an Hoescht A. G. approach to the scale-up and improvement of two organic electrosyntheses: the electrocatalytic dehalogenation of dichloroacetic acid and the electrochemical synthesis of hexa fluoro propylene oxide. The latter system performs the direct oxidation of the gaseous species on lead dioxide in a cylindrical membrane cell operating under pressure.

Chapter 6 offers two more organic electrosyntheses from Reilly Industry, described in terms of implementation and technology transfer from laboratory scale to production. The reduction of 2-methylindoline utilises the commonly used lead cathode while the hydrodimerisation of paroxypropione uses a zinc cathode.

Chapter 7 is an exposition of the development of the largest scale electro-organic synthesis the hydrodimerisation of acrylonitrile to adiponitrile. Aspects of scale-up, cell design, search for supporting electrolyte, pilot scale operation and the move to undivided cells away from membrane cells are described. Although important, electrochemists may well have seen this before in a number of books.

Chapter 8 shows that large scale electro-organic synthesis can be carried out in a non-aqueous solvent; dry DMF in this case. This synthesis of fenoprofen encountered scale up problems with the electrocarboxylation of the organic halide which caused a shift to a sacrificial magnesium anode in the form of a unique pencil sharpener cell design. Use of this anode technology could find wider use with aprotic solvents.

Chapter 9 is slightly different to the previous five chapters in dealing with experiences of continuous process operation of the desulphurisation of methyl benzyl sulphide to the toluene derivative. The particular focus of the chapter is the interaction of unit operations with the reactor function. This chapter originally appeared in *Electrochemical Cell Design* (edited by R. E. White) in 1984 which was published by Plenum.

Chapter 10, dealing with aromatic aldehydes, ketones and quinones by mediated electrooxidation, describes a claimed major development in the mediated oxidation of aromatic precursors using Ce (IV) as an oxidant. The GEMS process from Grace uses a new anion, methanesulphuric acid, with a higher Ce (IV) solubility and a resulting higher process efficiency. Eight samples of synthesis are cited, but little other useful information relevant to the book subject area is included.

Chapters 11 and 12 give separate accounts of inorganic electrosynthesis. The first of these gives performance details of bench scale operation of the production of chlorine dioxide, an alternative bleaching agent to chlorine. Scale-up is unfortunately not considered. The second example applies familiar halogen chemistry in the production of sodium bromate in a general purpose flow electrolyser, the DEM cell developed at the ERDC. Scale-up performance is described.

Chapter 13. The ICI FM01-LC Electrolyser for electrosynthesis promotes the use of this cell, originally developed for the chlor-alkali industry, as a general purpose unit. Apart from describing the unit there is little of interest to the reader which could not have been obtained from promotional bulletins from ICI.

Chapter 14 provides a practical account of considerations of anode design and how to engineer anodes from laboratory to pilot scale.

The final chapter is somewhat different to the others, giving an example of membrane technology in waste treatment and specifically the recovery of ammonium sulphate and sulphite emanating from a p-aminophenol plant. Although the process is a com-

bined electro dialysis and reverse osmosis operation, which gives the optimum process treatment achieved, it is something of a mis-match with the rest of the volume.

Overall the concept of the book is interesting and important but is, in truth, only partly addressed. The contents are somewhat unbalanced, there is no real linking between the chapters, some of which are far superior in content and treatment than others. This is clearly a result of the assembly of numerous lecture style presentations. An index to the volume is not given and would have been a useful addition.

On the positive side, there are some good qualitative accounts of scale-up of electrochemical processes. Surely this demonstrates that electrochemical technology can readily transfer from laboratory to production.

The book should be of interest to industrial chemists and chemical engineers and it is a welcome addition to the subject area. On a purely personal note I would have preferred to see a more ambitious work in which the science and the engineering are blended into the technology through design and economics.

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A first course in electrode processes

by Derek Pletcher

The Electrochemical Consultancy, £18.00 1991, pp. 274

Those of use whose professional task it is to inspire, coax and instruct undergraduate chemists with the hope of propagating tomorrow's electrochemists have long laboured under the handicap enforced by the absence of an undergraduate-friendly textbook of realistic length with which to complement our lecture courses. Equally as research supervisors we have been perplexed as to identify suitable beginning texts to initiate novice graduate students. Pletcher's new book goes a substantial way to meeting both these needs. Whilst unashamedly classical in content, the text has the essential merits of clarity of explanation and lucidity of construction. The reader is provided with comprehensive, extremely well-written but economical descriptions of the physical processes which control electrode reactions. Mathematical arguments appear where helpful, however they are simply presented and carefully rationed in quantity which perhaps reflects the author's experience as a contemporary British university teacher. The book has a good index, a very useful set of problems (with answers) and is largely free of errors.

Although much of the material covered is inevitably predictable — electron transfer, mass transport, adsorption, interfacial structure, cyclic voltammetry, electroanalytical techniques, etc — curiosities include the contraction of spectroelectrochemistry (which students usually find particularly stimulating) in just four pages, only a superficial outline of the merits of microelectrodes, the resurrection of the rotating ring-disc electrode and, astonishingly, no mention whatsoever of scanning tunneling microscopy and allied techniques or bioelectrochemistry! Exciting fundamental science is thus omitted and this is surely a missed evangelical opportunity. Instead we are given two chapters entitled 'The manufacture of Cl₂ and NaOH' and 'Man versus Corrosion'. Important though these technologies are, I doubt if their study at this level is likely to encourage young scientists to embrace our discipline. Nevertheless, overall, the depth of the book is generally well-judged and the quality of the explanation of the basic principles is very high indeed. I intend, at least for the time-being, to adopt this book as the major recommended text for the purposes mentioned above.

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Potentiometric Water Analysis (2nd ed.)

D. Midgley and K. Torrance,
pp. x + 586, John Wiley & Sons, Chichester,
New York, Brisbane, Toronto, Singapore,
£65.00, ISBN 0 471 929 832

Of the thousand or so scientific and technological books published every year, not a few copies end their days ignominiously by being pulped! And in recent years, more than a few publishers have held discrete "Sales" in an attempt to clear their warehouses of stock which has not sold and which appears unlikely ever to be so. That this substantial volume has been re-issued as a second edition speaks more loudly in its favour than any reviewer's comments.

The reason for its success, one would judge, rests on several factors. Most obviously, in this environmentally conscious age, water quality is a "hot topic". And not before time! For that, in a time when even those of the most modest means think nothing of having a colour TV, if not other electronic entertainment appliances, it is a scandal that so many of the great rivers of the world run so foul even to approach them is unpleasant.

Secondly, while advances have been made in the sophistication of all instrumental analytical methods, those based on electrochemical principles — electro-analytical methods — have probably benefitted most advances in microelectronic technology and the lowering of component prices in this field. Unlike, say, an atomic absorption spectrometer with its various specialised optical elements, the instrumentation used in potentiometry is assembled almost completely from "off-the-shelf" components.

Of course, in its very simplicity lies the greatest weakness of potentiometric analysis. At the end of the day, the user is measuring a potential difference. Even though the Nernst equation may suggest that this p.d can be used to measure concentration, there are many possible pitfalls. It would be a brave man, especially in a changing or poorly-defined situation, who claimed to be able to measure concentrations unequivocally by a simple single potentiometric measurement.

The authors of this volume are well aware of such dangers and the careful reader will benefit from their wisdom and hopefully avoid such pitfalls.

The contents of the volume are much as one would hope and expect. The basic principles are set forth and various different electrode types described, as are the instruments — call them electrometers — used with

the electrodes. The use of special pH boards in personal computers is covered here as is the "industrial" side — on-line process control. Chapter 5 is titled "Analytical Methods" and while this probably contains nothing new to the card-carrying analytical chemist, the tests it describes will, if carried out, protect the unwary from making a fool of themselves. Chapter 6 "Potentiometric Titrations & Related Methods" and Chapter 7 "Potentiometric Analytical Practice" continue the theme, though now in a more technique-specific environment as their titles imply. All of the foregoing account for 165 pages of this book. In Part II, we get to the red meat — nearly 400 pages of specific methods, starting with pH, going on through Li, Mg, Ca, Cd, Ag . . . with anions, and uncharged species such as carbon dioxide, chlorine and surfactants. These analyses are described — and this is not a criticism — on a "cookbook" basis. In each case, the equipment and reagents needed are listed, as is the concentration range of the method, sources of errors and — perhaps of greatest interest to the newcomer — comparison with other methods.

As far as one can ascertain, this volume contains everything pertaining to its subject. The index is generous and chapters are adequately referenced for those who would dig deeper. Because of its size, there is a certain danger that the impetuous practitioner might, in focussing on a specific analysis, overlook the more general wisdom set out in Part I. If this were to have adverse consequences, one could hardly blame the authors.

The book is strongly recommended for all with an interest in water or effluent analysis, especially for those concerned with industrial effluents such as those from the metal-working or metal finishing industries. The emphasis is on analysis of fairly low concentrations such as are found in effluent and less on the higher concentrations found in, say, electroplating. However all the facts are there to allow use of the methods for such concentrations, whether by their simple adaptation or by dilution of stronger solutions.

The authors are to be congratulated on their work and it is a matter of speculation as to whether, under the privatised regime which is now responsible for electricity generation in the UK, such a book could or would ever have been written. But that is another story!

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'Synthetic organic electrochemistry' 2nd edition, by Albert J. Fry, John Wiley and Sons, New York (1989) £43.20 ISBN 0-471-63396-8

This book is not a work of scholarship and may well be frowned upon by purist research supervisors who are *au fait* with the latest in synthetic and mechanistic electro-organic chemistry. On the other hand, like the

first edition, it may be widely read and consulted by postgraduate students and other entrants to the field. Better the imperfect book which is read than the perfect work which remains unopened.

Dr Fry has tackled a difficult task. The electrochemists are impatient with superficial accounts of their subject yet the organic chemists wish painlessly to be introduced only to a minimum of electrochemistry

and a maximum of know-how. For this book the organic chemists are the customers, and therefore to be pandered to. Yet they are notoriously conservative and usually turn to electrochemical methods when all else has been tried, and failed.

The approach here is conventional. Introductory chapters on electrochemical principles and techniques are followed by several which survey electro-organic reactions of practical significance. These are classified according to single bond cleavage, reduction of multiple bonds, reduction of conjugated systems, oxidation of carboxylic acids and aromatic compounds, and indirect electrolysis (electrocatalysis and electro-generated reagents).

The early chapters identify fairly well those electrochemical concepts and methods necessary for the pursuit of electrosynthetic applications. Inclusion of surface phenomena, adsorption, and the double layer is perhaps superfluous for the task in hand. Identification is one thing, clarity of discussion is another. The synthetically minded budding electrochemist will probably be confused by the early chapters. Linear sweep voltammetry is discussed superficially in three chapters; one, full, discussion would be better. There is also a confusing use of symbols, e.g. *V* is used variously for volts, volume, and (*italicized*) for sweep rate. The IUPAC convention is defied over the signs of cathodic and anodic currents although, in fairness, Dr Fry's usage is the one most commonly met in the electro-organic literature. A glossary of symbols could usefully be added.

There are many typographical errors. The introductory chapters are written in a verbose style with

overlong sentences and an overuse of parentheses. In contrast, the chapters dealing with examples of electrosynthetic transformations are more densely written. The choice of examples is good and the likely advantages of the method well-illustrated. These include selectivity, through potential or current control, and mildness of reaction conditions. Clear summaries of such features, together with tables of redox potentials of key functional groups, would help the beginner. Discussion of the mechanism is, however, out of date. There is scant acknowledgement of the predominance of DISP mechanisms over ECE. Intelligent beginners will wish to know such things as they seek to assess the applicability of a particular reported reaction to their own immediate synthetic problem.

The chapter on indirect electrolysis is very disappointing. It is too short to do justice to this increasingly important and relevant topic. The basis of redox catalysis should have been more fully explained and more up-to-date examples provided. It is not even made clear what constitutes a good mediator. Organic chemists are attracted by the possibility of using electro-generated reagents and electrocatalysis and this chapter is not sufficiently helpful.

The final chapter covers hardware and experimental method. This is a good idea and useful points are made. The key section of the principles of cell design covers the essential material but is not well-organized; a summary of key features would have helped greatly.

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