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NEWS

Book reviews

Electrochemical and electrocatalytic reactions of carbon dioxide Edited by B. P. Sullivan, K. Krist and H. E. Guard
pp. xvi + 298, Elsevier, Amsterdam, 1993
$212.50/Dfl. 340, ISBN 0 444 88316 9

Interest in the electrochemistry of carbon dioxide has greatly accelerated in the last two decades with concern about the energy crisis and the potential shortage of carbon–based feedstocks. Then as awareness of the greenhouse effect spread, ways of artificially fixing carbon dioxide were increasingly investigated. The principal approach to this problem has been via electrochemical reduction. Addition of one electron produces a carbon dioxide radical anion. This can react further in one of four ways: (i) further reduction to formate and on to formaldehyde, methanol and to methane; (ii) disproportionation to carbon monoxide and carbonate, with further reduction to ethene, ethane, propene and propane; (iii) dimerisation to oxalate and further reduction to glyoxylate, glycolate, tartrate and malate; (iv) addition to other substrates to form carboxylates.

The current book starts with a brief but competent survey of thermodynamic, kinetic electrochemical and product possibilities for carbon dioxide reactivity including reference to its co-ordination chemistry, which forms the topic of Chapter 2. Carbon dioxide binds to more than ten transition metal centres including W(II), Fe(O), Co(I) etc. The relationship is carbonyl complexes is carefully considered especially in relation to the water gas shift reaction: $CO + H_2O \longrightarrow CO_2 + H_2$. The theme of this reaction is taken up in more detail in Chapter 3 with special consideration of a range of catalysts – mostly involving carbonyl complexes but very few carbon dioxide complexes.

Chapter 4 is a fairly specific piece of largely unpublished experimental work on the concentration of carbon dioxide via quinone dianions. Although the work is interesting, it does not warrant a whole chapter.

The theme of transition metal complexes of carbon dioxide is resumed in Chapter 5, this time concentrating on transition metal catalysed electrochemical reductions. The style of this chapter does not make easy reading. It involves just one-carbon reductions.

Chapter 6 starts promisingly with electrochemical reductions on solid electrodes. Then the authors provide 30 pages of detail on their own work with copper and silver electrodes to form methane with some CO and ethane. The formation of methanol in good yields is mentioned and there is a passing reference to oxalate formation.

Chapter 7 covers some of the same ground as Chapter 6. It starts with a discussion of mechanistic studies related to voltammetric and photoemmision work and continues with product distribution studies. An important section then deals with electrode configurations promoting high rate reductions. The proposed mechanistic scheme is rather speculative and ignores the disproportionation and dimerisation routes.

Chapter 8 is a useful account of photoelectrochemical reductions, using ruthenium and rhenium bipyridyl based photosensitisers and with nickel cyclams, as well as semiconductor electrodes and powders. The formation of glyoxylate is mentioned.

It is always difficult with a multi-author volume to obtain a satisfactory balance of depth and breadth of coverage between the different chapters along with compatible styles of presentation. The editors of this book have done a good job in this respect. The book would have benefited from a longer introduction, and from a concluding chapter drawing together the various strands, and pointing to future areas needing development. Chapters 2, 4, 5 and 8 have their own summaries but unfortunately not Chapters 6 and 7. The subject index is satisfactory, but has no unusual layout. There is no author index. Overall it is a useful and important contribution to the state of knowledge of carbon dioxide reduction although there is little reference to dimerisation products or any of the relevant papers in *Tetrahedron Letters.*

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Advances in electrochemical science and engineering, Vol 3
Edited by Heinz Gerischer and Charles W Tobias
331pp, VCH, Weinheim, 1994
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The third volume in this established series contains five reviews, four of which are particularly relevant to the fabrication of materials and devices for the electronics industry.

Walter P. Gomes and Hans H. Goossens (Universiteit Gent, Belgium) consider the 'Electrochemistry of III–V compound semiconductors' with an emphasis on dissolution kinetics and etching. This field of semiconductor (photo)electrochemistry has blossomed since the 1970s when it was realized that the development of solar energy conversion systems using GaAs, GaP and InP was restricted by photocorrosion of the semiconductor materials. Alternatively, the deliberate and controlled dissolution of these materials (i.e., etching) has become an essential process in the fabrication of electronic devices. The authors provide a comprehensive treatment of anodic dissolution and etching and provide information on mechanistic and

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morphological aspects. The treatment emphasizes the underlying science rather than the technology of practical devices. There are 123 references, the latest of which is dated 1991.

'Electroless deposition processes: fundamentals and applications' are described by Yutaka Orinaka (AT & T Bell, retired, New Jersey) and Tetsuya Osaka (Waseda University, Tokyo). There have been many reviews of this subject since Brenner and Riddell coined the term 'electroless' plating in 1946 to describe the autocatalytic deposition of metal from a solution containing a reducing agent and the metal ions via a mixed electrode process. This chapter provides a valuable Japanese perspective on the development of the field and adopts an approach which focuses on the use of linear polarization, cyclic voltammetry and impedance techniques to provide an improved understanding of the fundamental process of electroless deposition. The use of cobalt alloy films as magnetic recording media receives particular attention as does the use of copper deposition in the printed circuit board industry. This timely and readable review has already found use in our laboratories but I was surprised to see no treatment of the development of composite deposits based on electroless nickel (or cobalt) and polymetric (e.g., PTFE) or hard (e.g., SiC) particles for the surface engineering industries. Some 206 references are provided the latest dated 1993.

John Dukovic (IBM Research Division, New York) provides a 42 page review of 'Current distribution and shape change in electrodeposition of thin films for microelectronic fabrication'. This is a well-written treatment which considers mathematical modelling and computer-aided modelling of current and deposit thickness distribution but technological examples of good and poor distributions and related production problems are not covered. Some 81 references are given, the most recent one being 1992-based.

'The principles and techniques of electrolytic aluminium deposition and dissolution in organoaluminium electrolytes' is reviewed by Herbert Lehmkuhl, Klaus Mehler (Max-Planck Institut fur Kohlenforschung, Mulheim a.d. Ruhr) and Uwe Landau (MIB GmbH, Berlin). This chapter is dedicated to the memory of Karl Zeigler (1898–1973) who pioneered much of the work in this field in the mid-1050s. Both plating and refining are considered and the emphasis is on the importance of the solution-based inorganic complex chemistry of the electrolytes. It was pleasing to see photographs illustrating important industrial applications in this field together with corrosion data for aluminium coatings versus competitive (e.g., galvanized) ones. Some 242 references are supplied, the last one referring to 1992.

The final chapter by Panayotis C. Andricacos and Lubomyr T. Romankiw (IBM Research Division, New York) treats 'Magnetically soft materials in data storage: their properties and electrochemistry'. This vital field is being driven by the ever-increasing demands for memory storage capacity and data acquisition/transfer speed. Commercial devices are currently approaching 30 megabits per cm^2 although laboratory trials have recently demonstrated rates up to 10^9 bits per cm^2. This review concisely describes working devices, such as recording heads and the selective deposition of Ni–Fe alloy (Permalloy) films using pattern techniques. The effects of electrolyte variables are discussed in some detail and theories for the anomalous deposition of nickel in these alloys are highlighted. Some 193 references are provided, the latest one referring to 1992.

To summarize, this volume contains five well-written reviews which should prove valuable to electrochemists and other workers, particularly in the field of microelectronics fabrication and the production of data storage materials. My postgraduate students are already commenting favourably on the material. On a personal note, I would have preferred all chapters to contain a balanced treatment which integrates *engineering* and scientific aspects of the subject while providing information on the *industrial applications* in each case.

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