

NEWS

Book reviews**Photocatalytic production of energy-rich compounds**

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Proceedings of Second EC Workshop on Photochemical and Photobiological Processes for the Production of Energy-Rich Compounds, Seville, Spain, 22-25 September 1987.

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This book falls squarely between two stools, being neither an introductory textbook or a comprehensive review of the relevant literature. Rather, it is a curious cross between the two and therein lies its main strength. Conceived in part, as a summary of the progress made in research projects funded by the Commission of the European Communities, the cross-disciplinary nature of the work presented also makes it of interest to a wide variety of scientists, active both within the field and in ancillary subjects.

The content of the book is divided up into four well-defined sections: "Presentations by EC Contractors" (which might very well have been called "Introduction"), "Photochemistry", "Photoelectrochemistry" and "Photobiology". Grassi and Hall have performed a real editorial balancing act in the sequence in which the papers are presented: a novice may start at page one and work his or her way through and acquire a broad but incomplete grounding in the topics discussed, while the old lag in the field may dip in and obtain a greater perspective on the relevance of his own research, as well as a considerable body of useful references.

The first section serves as an introduction to some of the methodologies adopted in photocatalytic energy conversion. Mackor *et al.* discuss the synthesis of binuclear cobalt complexes for the photoelectrochemical reduction of carbon dioxide. Porter and Giorgi and Mathis, in their two papers, make the first mention of the plant reaction centres PS-I and PS-II and acquaint the reader with the main techniques (flash absorption and fluorescence, EPR) used in the analysis of their structure and composition, and the elucidation of the primary redox reactions involved in efficient light-induced charge separation. Hall, Evans and Grätzel discuss various strategies used in the development of bacteria and semiconductor-based immobilized photosynthetic systems with activities comparable to those found in free-living cells.

Section two, entitled "Photochemistry", is the largest in the book and concerns itself primarily with investigations into the fundamental processes of various photosynthetic analogues and the develop-

ment of a model for photosynthesis in plant. The photosynthetic analogues discussed fall broadly into two types: those that are dye photosensitizer based, and those that employ large band gap semiconductors, usually in the powdered or colloidal state. Michael Grätzel and his co-workers manage to touch both bases with an easily-digested paper on titanium dioxide sensitization with metal cyanide complexes, while Munuera *et al.* drive another nail into the coffin of the quest for cost efficient light induced water-splitting with a paper on oxygen-suppressed hydrogen production on metal/titanium dioxide polycrystalline powders. Verhoeven *et al.* abandon the search for alternatives, however, with a paper detailing their efforts to reconstruct the necessary functionalities present in PS-II and so put plant-based photosynthesis on a more quantitative basis.

Section three is called "Photoelectrochemistry" and, in keeping with the sequential nature of the book, succeeds agreeably from section two. Working from an electrochemical point of view, it is concerned entirely with the study of light-induced reactions on semiconductors and, in one paper by Jaegermann, tries to correlate observations related to the semiconductor-electrolyte interface with those obtained from UHV surface spectroscopic techniques such as XPS, ISS and LEED: this is especially interesting as, as Meissner and Memming remind us in a paper on the effect of the presence of inter-band states at the semiconductor-electrolyte interface, the nature of the semiconductor surface determines the properties of the system as a whole. Mention is again made, in a well considered paper by Salvador, of the photolysis of water, this time with the objective of hydrogen peroxide production.

The last section is entitled "Photobiology" and as such is most concerned with the useful photosynthetic/photochemical implementation of naturally occurring materials: De la Rosa, for instance, reports the use of PS-I and PS-II, isolated from supermarket purchased spinach, in the photogeneration of hydrogen peroxide. Of the four, however, this section is the most eclectic in the variety of material presented ranging, for instance, from the chemical kinetics of Wollman and Lemaire's somewhat truncated discussion of the role of phosphorylation in the control of balanced PS-I and PS-II photoexcitation in plants, to the investigation of Guerrero *et al.* into the optimum conditions for useful biomass recovery from nitrogen-fixing blue-green algae. On the whole though, this section has the most up to date coverage of the literature presented in the various papers, especially those relating to PS-I and PS-II.

In summary, the greatest strengths of this book are the breadth of the material it covers and the sequence in which it is presented; its greatest weaknesses are

some pretty appalling typos and that no one topic is covered in detail but, as mentioned in the introduction, this is entirely due to the book being, effectively, a conference report and on that level it succeeds admirably. At £29 a copy for the hardback edition, this book is almost a bargain; thus, if you are at all interested in the field and enjoy a distracting read, why not buy it?

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Electrochemistry

Philip H. Rieger, Prentice Hall, Englewood Cliffs, New Jersey,
ISBN 0-13-249138-9
£17.95, 528 pages.

"Electrochemistry" is a textbook at the Honours Degree level covering most of the material that would be required in a traditional physical chemistry course on the subject. Some of the coverage is eclectic: the author makes it clear in his unusually frank preface that the book has, like Topsy, just grown. It is an amalgam of several rather disparate lecture courses, with the result that areas such as colloid chemistry and organo-metallic electrochemistry are covered in considerably greater detail than would be customary in books of this sort. The ordering of the material is also unusual, at least in part: the first chapter, for example, ostensibly on thermodynamic aspects of electrochemistry, contains a discussion of fuel cells that wrestles uncomfortably with the most important property of these devices; their non-thermodynamic behaviour.

There are other infelicities in terms of ordering of material in the first two chapters. Activities and activity coefficients are introduced very early in the first chapter, in order to allow the Nernst equation to be quoted in a rigorous form and to permit the definition of the formal potential. In fact, the remainder of this chapter moves rather uneasily between activities and concentrations, and at no point is any quantitative theory of activity evoked until the end of chapter two, where it appears almost as an afterthought to the main account of the electrified interface. It is not obvious why this is done and it would have been far better to have incorporated an essentially equilibrium solution theory into chapter one.

The main part of chapter two is focussed on the electrified interface. After a brief discussion of the Poisson-Boltzmann model, Rieger then presents a lengthy and interesting digression into the properties of colloids, before returning to electrocapillarity as a phenomenon of macroscopic electrodes. The treatment of electrokinetic phenomena is unusually detailed and serves as an admirable introduction to this field, though inevitably there is little opportunity to present recent work in this area.

The third chapter reviews electrolytic conductance. For the most part, the treatment is conventional and

uncontroversial, and concludes with a good discussion of membrane potentials. The fourth chapter builds on the third, and at the same time moves us into the area of practical electrochemical measurements by concentrating on reversible systems. Again the author follows standard practice, dividing the treatment of electrochemical systems into two aspects: those governing transport of reactant to the electrode and those involving electron transfer at the interface. Transport of reactant and product is not dealt with at any length; solutions of the diffusion equations are quoted rather than derived, though an appendix does give some indication to the more mathematically curious of how such solutions might be obtained. The section on practical methods is not particularly transparent; an understanding of the principles of operational amplifiers is not vouchsafed to all undergraduates, and the discussion of the potentiostat in chapter four will prove far from easy to understand. Also likely to be difficult is the subsequent treatment of potentiometric titrations, described in terms of the zero-current pathway on a three-dimensional $i/X/E$ surface. By contrast, the treatment of cyclic voltammetry is very cursory, a matter for some regret given the current very widespread and often uncritical usage of this technique in the literature. The final sections of chapter four cover polarography, RDE studies and applications of these techniques to the exploration of solution equilibria and analytical studies, and are very good.

Chapter five tackles the core of modern electrochemistry, the electron transfer process at the electrified interface. As such, it forms the backbone of the book, and the treatment of the fundamentals is reasonably thorough without being overwhelming. The extension to more complex electrochemical reactions is quite clear, and several examples are given. There is an involved section on irreversibility in voltammetry that will repay careful reading, and a section on faradic impedance that, in its efforts to avoid complex number theory, ends up unhelpfully quoting results that the reader will find difficult to generalise. The final sections of chapter five, on mechanisms of electrode processes, are very good, and integrate electrochemical reactions very well into the framework that will be familiar to most chemists from courses on organic and inorganic reaction mechanisms.

The final chapter is entitled electrolysis and reviews a variety of electrochemical processes including some of those used commercially, both inorganic and organic. The book concludes with a brief discussion of that most ill-understood of all electrochemical phenomena, corrosion. The treatment is very basic here; no coverage of pitting is provided, and recent work in the area is all but ignored.

The strength of this book is undoubtedly in the plethora of examples of electrochemical processes, particularly those reviewed in the last two chapters, which will commend it to many who wish to use the straight-forward electrochemical techniques described to explore the sometimes complex organic and

inorganic electrode processes currently of interest. It will also give undergraduate physical chemists a good basic training in, and understanding of, classical electrochemical techniques. Its weakness is undoubtedly the decision taken by the author to exclude all modern spectro-electrochemical techniques, with the result that the reader is deprived of an introduction to one of the most rapidly growing areas of electrochemistry. I very much hope that Dr. Rieger can be induced to

supply a second edition in which these techniques receive serious discussion; within the limits indicated above, the structure of the book is very sound and, suitably modified, it could become an even more useful addition to our bookshelves.

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