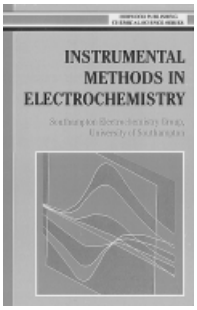
Current Affairs

Electrochemical Methods. Fundamentals and Applications (2nd Edition). By *Allen J. Bard* and *Larry R. Faulkner*. John Wiley & Sons Inc., New York 2001. 833 pp., hardcover £ 33.95.—ISBN 0-471-04372-9

Instrumental Methods in Electrochemistry. Edited by Southampton Electrochemistry Group. Horwood Publishing, Chichester 2001. 443 pp., softcover £ 30.00.—ISBN 1-898563-80-2

In 1980 the gaping lack of a textbook covering experimental electrochemistry in a complete overview, including both fundamentals of methods and experimental details with typical results, was closed very successfully by the first edition of the book by Bard and Faulkner. Both authors had established a well-founded reputation as electrochemists, and this was quite clear also in their textbook. That volume is certainly still used in many places as a standard reference by the electrochemical novice and the expert alike. Some new methods already in their infancy at the time of publication were mentioned only briefly, but that is certainly appropriate for this kind of textbook.



A few years later, in 1985, a second textbook of fairly similar scope and layout was produced by the Southampton Electrochemistry Group. Based on a postgraduate laboratory course at the University of Southampton, which had been a regular part of the lecture program since 1969, the team of authors seemed to guarantee a broader scope of experimental knowledge—a wider overall perspective. Consequently—and this is certainly no surprise with multiauthor books—this volume was somewhat more disjointed. Since it was published at a time when nontraditional methods, in particular in spectroelectrochemistry, were making rapid advances, this later volume provided a useful complement to the work by Bard and Faulkner.

Several years have passed since those first editions, more than twenty in the case of the book by Bard and Faulkner. Despite the somewhat depressing outlook in electrochemistry in some places, rapid developments and numerous advances have occurred on some fronts. Thus a new textbook or a thorough revision of the already established ones was overdue. Bard and Faulkner present a considerably enlarged second addition, with several new chapters and numerous additions to existing ones. The textbook of the Southampton Electrochemistry Group has been "republished" (whatever that means; although standard dictionaries do not define this term, it presumably amounts to reprinting). The books differ considerably in size (Bard and Faulkner offer 833 pages, whereas the Southampton Electrochemistry Group exercises some self restraint with 443 pages, exactly as in the first printing). Thus one purpose of this review is a careful comparison, ending in an admittedly subjective personal rating by the reviewer.

A review of the book by the Southampton Electrochemistry Group could be provided by simply listing references to the reviews published on the occasion of the first publication in 1985 (e.g., in *Ber. Bunsenges. Phys. Chem.*), because this book is a completely unchanged reprint of the first issue. However, as many readers will not have a copy of one of the earlier reviews, a brief review is provided below. The inherent weaknesses of the book still remain, but now it suffers further from the lack of any improvement and amendment, in particular with respect to modern developments and trends.

The book starts with a general introduction to concepts of electrochemistry. Actually this chapter is a collection of examples of electrochemical processes and the various steps they are composed of, also including some experimental methods. The second chapter deals with steady-state and potential-step techniques. In a rather unsystematic way (which is especially regrettable in a textbook), hydrodynamic methods, transient techniques, and microelectrodes are mixed up—to give just a few examples. Only a few lines on microelectrodes seems to be short shrift. This might have been appropriate in 1985 (some doubts remain) but in 2001 it looks miserly. A section on electron transfer follows. A good idea—but why spend a further 10% of a book about experimental methods on fundamentals and theory? The following chapter on convective diffusion systems is limited to rotating electrodes. Other experimental approaches—turbulent pipe flow, channel electrodes—are not even mentioned. Chapter 5 is devoted to the "electrical" (better: electrochemical) double layer. It provides a good introduction to this very fundamental topic, but only six of 29 pages are devoted to experimental methods for double-layer studies. Unfortunately these methods were already old fashioned in 1985: who still measures the interfacial impedance with an AC impedance bridge? Cyclic voltammetry and related techniques are treated in detail in the following chapter. As well as a broad introduction, some experimental aspects are treated, and even potential

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pitfalls (*IR* drop, double-layer charging) are addressed. The importance of numerical simulation for a qualitative understanding of a measured CV plot and for the extraction of quantitative kinetic data was certainly realized even in 1985, but in the absence of powerful computers and software complete simulations were impossible. The simple simulation programs provided in the first edition were certainly helpful; their presence in a book printed in 2001 causes mild humor.

A short treatment of electrocatalysis is provided in Chapter 7. Reactions evolving hydrogen, oxygen, and chlorine are treated in some detail. Experimental aspects are not discussed. Chapter 8 deals with AC techniques, that is, AC impedance measurements and AC polarography. Various methods used for impedance measurements are described carefully. Polarography is discussed only briefly. Numerous examples will help the newcomer. Chapter 9 on electrocrystallization has basically the same weakness as Chapter 7: not much on experimental aspects, some general introduction.

Chapter 10 on spectroelectrochemistry provides a reasonable overview of the state of the art in about 1982, but nothing beyond. Lastly, Chapter 11 on the design of electrochemical experiments is certainly a highlight of this book. Many students, even established researchers, from time to time wonder about experimental difficulties and clearly erroneous results. Sometimes a helping hand and mind are around, but when that is not the case this chapter might provide some ideas for troubleshooting. In the appendix, analytical and computational methods for the interpretation of electrochemical data are reviewed. This might somehow approach numerical simulation—a generally established procedure for evaluating cyclic voltammograms, etc.—but the term is not even mentioned in the index.

In conclusion, evidently republishing means just reprinting (or rehashing), and this is not a good idea in a rapidly developing field.

Bard and Faulkner clearly spent considerably more time and effort on their second edition. Although the number of pages was increased only by about 15%, quite a few chapters are clearly either completely new or at least substantially changed. This applies to electrochemical (traditional) as well as to spectroelectrochemical (nontraditional) methods.

This book too is certainly a mix of introductory electrochemistry textbook and laboratory guide. Nevertheless, it is well organized, so that the reader already familiar with basic concepts of electrochemistry, reactions, catalysis, etc. may just skip the introductory Chapters 1 to 4. Potential-step and potential-sweep methods are treated in two following chapters. Starting with a brief overview, techniques are described, including the necessary mathematics and practical advice. Polarography in its numerous methodological variants is treated in a separate chapter. It seems reasonable to keep the scope of this chapter just below the level of a monograph on analytical applications of polarography, as numerous specialized books on exactly this topic are available. Galvanostatic and coulostatic methods are the subject of Chapter 8.

Forced convection at rotating electrodes and at microelectrodes is described in Chapter 9. Modulation techniques are included, even electroosmotic flow is discussed. Turbulent pipe flow and other types of controlled convection are not even mentioned.

AC methods are collected in Chapter 10. A brief introduction again does not go beyond the bridge circuit, but fortunately the more modern instrumentation employed nowadays is described with sufficient detail towards the end of this chapter, after a detailed review of AC circuits and their components. These include approaches to obtaining kinetic data from impedance measurements. Some comments on the limitations of the methods are included. The treatment of AC voltammetry and AC polarography (which might, however, have been included in Chapter 7 on polarography) includes measurements of higher harmonics and the application of AC voltammetry in chemical analysis.

Chapter 11 on bulk electrolysis methods collects together various techniques such as electrogravimetry, coulometry, and stripping methods employed in analytical applications. Various types of flow cell, even those employed in detection systems for chromatography, are included. A special section is devoted to thin-layer cells. These cells are of considerable importance for traditional electrochemical methods such as cyclic voltammetry and various step methods; they are also frequently encountered in spectroelectrochemical setups. Somewhat inconsistently, and in an unnecessarily disjointed way, electrode reactions coupled with homogeneous chemical reactions are treated extensively in Chapter 12. Cyclic voltammetry and chronopotentiometry are discussed as preferred methods for studying such reactions, and therefore the content of this chapter might have been placed within the relevant chapters on either family of methods.

The chapter on double-layer structures and adsorption combines a thorough introduction to the topic with numerous results of experimental investigations aimed at the verification of the models developed to describe the double layer, its structure, and its dynamics. Even the effect of inert adsorbates on the rate of electrode reaction is included, with appropriate reference to the experimental method used to study this effect. Electrodes modified by any kind of surface treatment or deposition of additional material are treated in the following chapter. Numerous examples include covalently attached redox-active species, redox-active polymers, intrinsically conducting polymers, and a broad variety of inorganic films. Sometimes the chapter briefly develops into a review on these electrodes, but the authors never succumb to the temptation and always return quickly to experimental aspects of the respective investigations. In particular, cyclic voltammetry with these electrodes, the method that is most often used, is discussed in detail.

Electrochemical instrumentation is the subject of Chapter 15. After carefully reading this text the electrochemist will understand the various functions of a potentiostat and—what is certainly most important—will be able to use the instrument properly. Some suggestions for troubleshooting and detailed electronic circuitry to be used with microelectrodes are included. Unfortunately the use of the circuit diagram is somewhat limited: the most important part (an operational amplifier) is not produced any more, and replacements are hard to find. In addition the actual capabilities of this current transducer are somewhat limited. With

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an amplification factor of 10^4 it is hardly conceivable that one could measure currents in the picoampere range. Perhaps this device was intended to cooperate in a way not explained here with the current follower of the attached potentiostat. This problem is a general one, most authors prefer to treat any instrumentation as a black box. It is fair to say that in most cases the average researcher will not have the necessary background in electronics to apply detailed information appropriately.

Scanning probe techniques (Chapter 16) and spectroelectrochemistry (Chapter 17) are certainly the areas where there have been the most breathtaking advances as compared with the first edition of this book. It is entirely reasonable to limit the treatment to scanning tunneling microscopy (STM), atomic force microscopy (AFM), and scanning electrochemical microscopy (SECM), with impressive samples of actual results in the former chapter. Spectroelectrochemistry is somewhat harder to organize. Except for some electron spectroscopies (Auger electron spectroscopy, etc.), the authors limit themselves to in situ methods. Methods that are mentioned very often, such as UV/Vis and vibrational spectroscopy, or methods where the authors have been involved themselves (electron spin resonance spectroscopy), are described in detail with a wealth of practical information. Other methods such as surface plasmon resonance, ellipsometry, and second harmonic generation are also covered adequately. Somewhat surprisingly, the quartz microbalance shows up, whereas Mössbauer spectroscopy and circular dichroism are missing. This is certainly not a major drawback—spectroelectrochemistry is an extremely broad field that is difficult to cover in an appropriate way. The selection provided here is adequate, and according to publishers' lore a book devoted entirely to spectroelectrochemistry and surface analytical methods will be published soon by Springer. One missing detail—photoemission, in particular from metal electrodes—is briefly mentioned in the final chapter (18) on photoelectrochemistry. This chapter provides a mixture of an introduction to semiconductor electrochemistry and photoeffects at semiconductor/electrolyte solution interfaces. Experimental aspects are also treated, but because the experimental setups are either very complex or extremely simple, not much detail is given.

The illustrations are numerous, carefully designed, and of high quality. Somewhat confusing is the inconsistent labeling of the axes in current–potential plots. Certainly the tradition of polarography merits some attention, but there is certainly no need to apply polarographic thinking to the current–potential curve of the system $Pt/HBr + H_2O/AgBr/Ag$, whereas otherwise CVs are plotted in the way that is generally accepted. Quantity calculus has not been used in the labeling of axes; this should not have happened in a textbook which will sometimes need to provide very detailed guidance for students.

The treatment of mathematical methods and digital simulations in the appendix is limited to a few examples and only one remaining FORTRAN program. References to standard software are provided in an appropriate way. The list of electrochemical data at the end is helpful, although the wrong value of the potential of a Hg/HgO reference electrode on the back page has not been corrected.

All the chapters are as carefully organized as the whole book. Clearly the authors had as a concept in mind to provide at least some guidance for the average reader, without being too patronizing. An extensive list of symbols and abbreviations and a long index provide further assistance. Problems are given at the end of every chapter. This is standard fare in American textbooks, but is rarely encountered in European textbooks. The use of problems is subject to different opinions; without proper answers and/or solutions provided elsewhere, their practical value is somewhat limited anyway.

In conclusion: assuming the reviewer may spend a few pounds on a new book for the electrochemistry laboratory, he will do so by buying the amazingly rejuvenated Bard and Faulkner volume.

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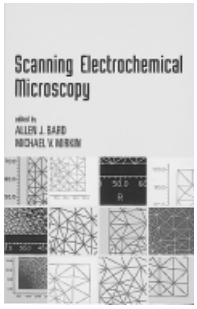
Scanning Electrochemical Microscopy. Edited by *Allen J. Bard* and *Michael V. Mirkin*. Marcel Dekker, Inc., New York 2001. 650 pp., hardcover $ 195.00.—ISBN 0-8247-0471-1

When, about ten years ago, Allen J. Bard and Daniel Mandler proposed the idea of scanning electrochemical microscopy (SECM), no one could envisage the wide variety of problems to which this technique is now being applied. As well as being a further addition to the range of scanning probe techniques for the imaging or modification of surfaces, extending these into the domain of electrochemistry, the method has been shown to have a much wider potential. It has opened up previously unimaginable possibilities for the microscopic study of biological systems and of the kinetics of electrochemical reactions at solid–liquid and liquid–liquid interfaces. This monograph edited by Allen J. Bard and Michael V. Mirkin is the first comprehensive survey of these developments that have occurred during the last decade, and goes far beyond the scope of the few review articles that have appeared.



The book begins with an introduction by Bard in his usual clear style, explaining the basic principle of SECM in a way that the general reader can understand. This is followed by detailed chapters on the construction of the microscope (D. O. Wipf) and the preparation of the microelectrodes (F. F. Fan and C. Demaille), with much practical advice for the experimentalist. F. F. Fan then gives a broad survey of the imaging capabilities as applied to many different systems, and M. V. Mirkin explains the theoretical fundamentals of the imaging mechanism in greater depth. This part of the book covering the foundations of the subject is rounded off by chapters on the application of SECM to measurements on the kinetics of homogeneous and heterogeneous reactions by K. Borgwarth, J. Heinze, and P. R. Unwin.

Applications to liquid–liquid interfaces are then discussed by M. V. Mirkin,

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