Comprehensive Modern Electrochemistry

MODERN ELECTROCHEMISTRY, SECOND EDITION, in 3 Volumes
Volume 1 IONICS, 1998, 767 pages
Volume 2A FUNDAMENTALS OF ELECTRODICS, 2000, 763 pages
Volume 2B ELECTRODICS IN CHEMISTRY, ENGINEERING, BIOLOGY AND ENVIRONMENTAL SCIENCE, 2000, 514 pages
BY J. O'M. BOCKRIS AND A. K. N. REDDY (AND M. GAMBOA-ALDECO, Volume 2A)
Plenum Press (Volume 1), Kluwer Academic/Plenum Publishers (Volumes 2A and 2B), New York, 2001
Set ISBN (hardback) 0-306-46597-3; (paperback) 0-306-46598-1, $ 115

"Bockris and Reddy", as it is usually called, has always been an acquired taste (1). Thirty years ago, as a newly appointed lecturer in Southampton, I was faced with the task of putting together a new M.Sc. lecture course in Electrochemical Science. Electrochemistry was then (and mostly continues to be) a Cinderella subject at undergraduate level, and so I was looking for a text book that was strong on fundamentals and that managed to convey the excitement of electrochemistry. As a postgraduate, I had grown up with Paul Delahay's two books, "Double Layer and Electrode Kinetics" and "A New Instrumental Methods" (2, 3). These were elegantly written (and astonishingly expensive), but, it must be said, a dry read. The first edition of Bockris and Reddy appeared in paperback in 1973, and I bought both volumes and started to prepare my course.

In retrospect I feel sorry for my M.Sc. students, who had to suffer my legendary express delivery peppered with explanations of Gaussian boxes and the Poisson-Boltzmann equation. I am glad to say that most of them went on to careers in electrochemistry, in spite of what must have been a terrifying introduction. What had captured my imagination at that time was the style of the book. In a way that was reminiscent of "Feynman's Lectures in Physics" (which I was reading at the same time) (4), Bockris and Reddy took their time with each topic and gave the background physics where appropriate. This appealed to me as a nascent lecturer. Whether my students found the two volumes so appealing is questionable. Certainly none of my colleagues at that time appeared to share my enthusiasm for the book; most regarded my desire to 'get back to basics' as mildly unhinged.

The two paperback volumes of Bockris and Reddy with their characteristic red and white covers have been on my shelves now for nearly thirty years. I had always felt that it would be an excellent idea to bring them up to date while maintaining their informal and entertaining approach, and so I was glad to be given an opportunity to review the new edition for *Platinum Metals Review*.

In spite of the rather specialist nature of *Platinum Metals Review*, it seemed to make little sense to me as a reviewer to comb through the books looking for references to platinum group metals. Of course, there are references to platinum, as a result of the central role that platinum plays in electrochemistry, most notably in electrocatalysis. Specialist interests aside, there is so much to read in these three volumes that no review can deal with all the areas covered.

Updating the First Edition

In terms of style, the enthusiasm and ebullience that characterised the first edition are still evident. The text flows easily, and the reader is pulled into each topic as the narrative develops. It was only as I got deeper into the book that I began to have serious misgivings.

The idea of a second edition raises the question – how does one update a book of this kind? Certainly by eliminating redundant concepts and updating theoretical and experimental aspects. This can be done relatively easily. However, as the authors stress in the introduction, this is a text book and a central issue for such a book is comprehensibility – a modern student must be able to follow the arguments without being side-tracked by irritating inconsistencies. Revision at this level is thus not an easy task.

The main problem, which the authors seem to have ignored for some reason, is that new generations of science and engineering students have only been educated to use SI units. The old Bockris and Reddy was full of dynes and esu, so one of the first things I would have expected the authors to do is to update the book to SI units and make it entirely consistent throughout. The authors have not done this. Instead, the reader encounters a bewildering mixture of equations with and without $4\pi\varepsilon_0$ scattered throughout the text.

A quick survey of postgraduates and of academic colleagues in Physics revealed in the former case complete ignorance of the use of esu in electrostatics and in the latter case astonishment that anyone would use them in a modern text book. Who knows what a Debye is in esu·cm? One cannot argue that the question of units is unimportant; on the contrary clarity over units is essential to any pedagogic endeavour. How else can students tackle the many numerical problems that have been included?

For example, any student using the electrostatics equations in Volume 1, will be completely baffled when attempting to use the equations. Neither the numbers nor the units will make sense. The student may search in vain for guidance in the list of symbols at the front of the book, but I could find no definitions of the relationships between unit systems. Since no answers to the problems are provided, one can only speculate how students taking a course on which the book is based might answer them.

Therefore, after spending several weeks browsing through the three Volumes, I concluded that the problem of unit systems would effectively preclude use of the books in any postgraduate course, let alone an undergraduate course. Units aside, these are fascinating books to read.

Volume 1: Ionics

Volume 1 maintains its clear approach to ionic solvation and electrolytes. It has been enhanced by a very extensive chapter on ionic liquids, including room temperature molten salts. The subjects covered in the Volume 1 have received very little attention in recent text books on electrochemistry. There are several reasons for this neglect. One is the emphasis on electroanalytical chemistry and interfacial chemistry that characterised the development of electrochemistry in North America after the 1960s. This has inevitably moved the subject away from its roots in European physical chemistry. For this reason alone, the appearance of this new volume is to be welcomed, even if a cautious approach to the units is required.

Volume 2

Volume 2 retains its original use of the term 'electrodics', a word that my spell checker is reluctant to accept and which I am even more reluctant to add to it. (Electrodics is the electrochemistry of phenomena occurring at the surface of electrodes, particularly charge-transfer reactions.) The content of the original Volume 2 has here been rewritten extensively and supplemented by a wide range of new material. For this reason Volume 2 is now split into two separate books: Volumes 2A and 2B.

Volume 2A: Fundamentals of Electrodics

This volume deals with fundamentals, whereas, in line with its title, Volume 2B deals with applications in chemistry, engineering, biology and environmental science. Volume 2A weaves its way through electrode processes in a rather eccentric, but nevertheless entertaining and generally informative way. While this is certainly not a reference text, it does have good moments for the jaded reader. Who, for example, can resist the information that Butler whistled softly to himself during his frequent periods of introspection, but was known on occasion to instruct nearby colleagues to be quiet? Or that Max Volmer's student, Erdey-Gruz later became Minister of Education in Hungary? With these morsels of historical insight appearing frequently throughout the book, it was not long before I started to read the footnotes before the main text.

New sections have been added that deal, in particular, with the structure of electrodes and the use of single crystals. The section on electron transfer is interesting, not least because of the way in which it marginalises the contributions of Rudi Marcus. His Nobel Prize award (for Chemistry in 1992 for

contributions to the theory of electron transfer reactions in chemical systems) suggests that a more balanced view would have been possible.

Volume 2B: Electrodics in Chemistry, Engineering, Biology and Environmental Science

And so to Volume 2B, the third book in this ambitious trilogy. Here the standard is patchy. Chapter 1, which purports to deal with photoelectrochemistry is particularly poor. There are several excellent text books on semiconductor electrochemistry, notably those by Morrison (5) and by Pleskov and Gurevich (6). Even Bard and Faulkner give a reasonable summary (7). By contrast, Chapter 1 is an odd mixture of experimental results and misleading theory. The peculiar expression for the photocurrent efficiency is incorrect, and the treatment of photocurrent voltage characteristics ignores half a decade of research.

A brief survey of 'organoelectrochemistry' follows. This omnibus title extends beyond electrode reactions involving organic molecules to consider topics such as conducting polymers. The award in 2000 of the Nobel Prize in Chemistry to Heeger, MacDiarmid and Shirakawa (conducting polymers) was a clear recognition of the maturity of the chemistry and physics of conducting polymers. However, this chapter does not do justice to the state of knowledge about these materials; for example, the use of 'semiconductor' models to describe the behaviour of the non-conducting state is deeply misleading.

After this unpromising start, the third volume improves substantially with good solid sections on corrosion, fuel cells and batteries. (One feels that the authors are more at home here.) The book concludes with sections on bioelectrochemistry and environmental electrochemistry, both topics that are centre stage in terms of potential applications in the 21st century.

In summary, these are three very reasonably priced volumes, with a total of over 2000 pages of text, which profess to comprise an undergraduate text. It is clear from the preface that the authors originally set out to write a comprehensive text book. In my view, what they have actually produced is rather different: something more like "A Treasury of Electrochemistry" – the sort of compendium that Victorians were fond of giving to their relatives for Christmas. At times the text is inspirational and notable for its depth of insight, at other times it is irritatingly lacking in presentational quality and balance. This is a text then with many strengths and many weaknesses; one that is suitable for a mature audience which knows when to take things *cum grano salis*, as my mentor, Heinz Gerischer, liked to say. Nevertheless, I found large parts of it a cracking good read, which is more than can be said for most text books.

References

1 J. O'M. Bockris and A. K. N. Reddy, "Modern Electrochemistry", in 2 vols., Plenum Press, New York, 1970 (hardback), 1973 (paperback)

2 P. J. Delahay, "Double Layer and Electrode Kinetics", Interscience Publishers, New York, 1965

3 P. J. Delahay and C. N. Reilley, "New Instrumental Methods in Electrochemistry", Interscience Publishers, New York, 1954

4 R. P. Feynman, R. B. Leighton and M. Sands, "The Feynman Lectures on Physics", in 3 vols., Addison-Wesley Publishing Co., Reading, Mass., 1964

5 S. R. Morrison, "Electrochemistry at Semiconductor and Oxidized Metal Electrodes", Plenum Press, New York, 1980

6 Yu. V. Pleskov and Ya. Gurevich, "Semiconductor Photoelectrochemistry", Consultants Bureau, New York, 1986

7 A. J. Bard and L. R. Faulkner, "Electrochemical Methods", 2nd Edn., Wiley, New York, 2000

L. M. PETER

The Author

Laurence Peter is Professor of Physical Chemistry at the University of Bath, U.K. His main interests are currently in semiconductor electrochemistry and photoelectrochemistry, including novel solar cells.

Platinum Metals Geoscience Publication

Special Volume 54, from the Canadian Institute of Mining, Metallurgy and Petroleum (CIM), on "The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements" will be published in Spring 2002.

This sequel, to Special Volume 23 published in 1981, contains new information on pge deposits worldwide in terms of geological setting, ore controls, mineralogy, geochemistry, mineral processing and beneficiation. The book can be ordered from CIM, 1210–3400 de Maisonneuve Blvd. W., Montréal, Québec, Canada, H3Z 3B8; Fax: (514) 939 2714. Website: http://www.cim.org/geosoc/SV_54_Form.pdf (prepublication prices until March 31st).