BOOK REVIEW

R.G. Compton and C.E. Banks, Understanding cyclic voltammetry

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Cyclic voltammetry has been established as the electrochemists' workhorse in laboratories all over the world for many years already. It is used to determine thermodynamic and kinetic data of all kinds of matter showing electrochemical activity (i.e., having sites which can be either reduced or oxidized or even both), to identify electrocatalysts for numerous applications, to establish operating conditions for spectroelectrochemical studies, to elucidate electrochemical reaction mechanisms, etc. This broad range of applications has attracted the curiosity of numerous researchers in other fields. Starting with those working in analytical, organic, and inorganic chemistry, the range of followers has expanded deep into materials sciences, biology, and even medicine. This broad scope of interested users unfortunately has two dark sides: a brief look into publications in journals of inorganic and organic chemistry containing results of cyclic voltammetry demonstrates how insufficiently the possibilities of the method are exploited—going straight down to obvious omissions and errors. Less visible is the second one: many scientists are convinced that electrochemistry can be done without electrochemists. In some countries, this has already resulted in dramatic losses of electrochemistry research groups at universities. The second problem can certainly not be solved with a book (although recipes of other kinds are always welcome); the first one may be addressed by a textbook starting at a very basic level. The present book apparently tries this approach—following in the tracks of previously published tomes like, e.g., the book: D.K. Gosser Jr.: *Cyclic Voltammetry*, VCH, New York 1993.

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The authors are active electrochemists themselves; R.G. Compton in particular is known for numerous contributions ranging from experimental developments and innovations over electrochemical thermodynamics to organic electrochemistry and materials science. As clearly stated in the preface, the book shall neither replace a monograph on cyclic voltammetry nor a reference book. Instead, it aims at the user with some basic knowledge of physical chemistry and only rather little knowledge of electrochemistry. Indeed the first chapter (out of nine) starts with basic concepts of thermodynamics as encountered in electrochemical equilibria. Very systematic indeed. But on p. 17, the reader starts to wonder seriously for the first time (after being somewhat puzzled about the rather unfamiliar use of empty brackets as symbols for unit concentrations on p. 3): In the middle of a discussion of the Nernst equation, a picture of Le Chatelier appears, and the following chapter is entirely devoted to W.H. Nernst, his life, his invention of an electric light, etc. This makes for entertaining reading—but does it make sense? Hardly! Instead, it appears to be one more illustrating case of an author, who wishes to put his very personal collection of knowledge and opinion into a book—without wasting too much time about the readers wishes, expectations, and desires. If such additions are really necessary for, e.g., a better understanding of the Nernst equation, it might have been added in an appendix—but in the present case, it will only stretch the readers patience. Following the statement, that a crater on the moon and several roads have been named after him, the authors return to the indeed important subject of reference electrodes—a subject treated on a preceding page already. A somewhat more systematic approach might have been a better way. Although an extensive treatment of the standard hydrogen electrode may be not really necessary in this book, it should be at least correct. The misspelling of Hückels name (not

Huckel) may be considered a nuisance, but for a standard electrode, the pressure of hydrogen gas must be exactly $p_0 = 101,325$ Pa and not close to 10^5 N·m^{-2}, the proton activity must be $a = 1$, a proton concentration close to 1 mol·dm^{-3} is hardly sufficient. Verifying the background—the Debye–Hückel limiting law and some further information of mixed phase thermodynamics—is a somewhat tedious task because the authors have assigned numbers to equations only when they thought it was necessary—searching for a particular equation is simply time-consuming. It nevertheless provides a nice opportunity for repetition: the equation $A \pm e \rightleftarrows B$ on p. 108 reappears on p. 110 as $A \pm e \rightleftharpoons B$. No big deal at first glance—but chemists are rather picky about the use of these arrows—and why repeat the equation anyway? While still pondering electrode potentials, the reader encounters a statement of a disappearing "In" term on p. 28. Some searching yields the place of the quoted equation—and the reader discovers somewhat amazed, that "In" refers to logarithm—and this is perhaps more adequately written as "ln."

Chapter 2 deals with electrode kinetics. The need for a three-electrode arrangement, the Butler–Volmer equation and the need for a supporting electrolyte are convincingly and well comprehensibly treated. Sections on the lives of Julius Tafel and—by all means—B. Stanley Pons and cold fusion are not exactly surprising anymore at this point but nevertheless certainly rather dispensable. Closely related to the charge transfer are diffusion processes, which are treated in chapter 3. Once again, the authors take the reader on a detour: how did A. Fick discover his laws?

Although the authors have touched upon the books subject from time to time in passing only in the first three chapters, cyclic voltammetry is in the focus of chapter 4. The first CV shown in Fig. 4.2 nicely illustrates the effect of the electron transfer rate constant on the appearance of the CV. But why is it necessary to multiply both axis with -1? Since just a few lines before the authors left the question open whether a reduction or an oxidation will be treated—apparently the former one proceeds—this question appears to be valid. A textbook should avoid confusion— and not create it. Some part of it is corrected on the following pages with additional information about the somewhat cumbersome activities of an IUPAC-panel of experts and the love of M. Branica for the Adriatic sea. Putting this minor (but because of the repetition by now boring) details aside the following pages contain the real message of the book: considerations regarding selection of potential limits, scan rates etc.—all these details so frequently overlooked in many of the papers mentioned above in the introduction. In the following chapter 5, the treatment is extended toward microelectrodes. Pitfalls and advantages of their use are eloquently treated, the selected examples are apparently very personal ones (see, e.g., the

sudden introduction of ionic liquids on p. 162). The smaller an electrode gets, the more important surface inhomogeneities may become. Consequently, heterogeneous surfaces are treated in chapter 6. The term is understood rather broadly, partially blocked electrodes, porous electrodes, microelectrode arrays, modified electrodes, and electrodes prepared from different materials (composites) are lumped together. Already, the first case—a partially blocked electrode—is almost too much for the authors. In an otherwise illuminating figure showing several CVs calculated for different sizes of the blocked surface spots, the reader will have serious difficulties associating the displayed traces with the spot size—and a typical parameter has a different symbol in the text and in the figure caption. The subsequently treated microelectrode arrays fare slightly better (although mircodisc on p. 211 is not a sign of careful writing) when their major advantage is stated: They provide a Faradic current response similar to a macroelectrode of similar mechanical dimensions at a drastically reduced capacitive background current. Somewhat unexpectedly (because not mentioned in the introductory overview of this chapter) electrodes made from highly ordered pyrolytic graphited (HOPG) are discussed next. Well—there are only two possible types of surface sites on this material: basal plane and edge sites. This could have been handled in a sentence instead of a section. To make their point (of heterogeneity), the authors add edge plane and basal plane HOPG and some boron-doped diamond and some glassy carbon—to illuminate their point that basal planes are poor electrocatalysts (it sounds strange to call them electrolytically inert on p. 219). The following very short sections cover other types and classes of heterogeneous electrodes without providing anything illuminating. Finally—after touching upon the both fascinating and exotic possibility of particle sizing with CV scanning electrochemical microscopy SECM is mentioned—but without showing a single CV.

Beyond the actual charge transfer preceding as well as following, chemical reactions may occur—and they substantially influence a CV. This feature—significant changes in the shape of a CV, striking dependencies on scan rates and varied values of scan limits—is presumably the most attractive one for many researchers outside the world of physical electrochemists. In a more systematic approach of such a book, this would have been an introductory picture —showing the whole process with all its conceivable steps (instead of meditating about craters on the moon). Well—it is never too late. Chapter 7 seems to be the place. The title is somewhat confusing: Cyclic voltammetry: Coupled Homogeneous Kinetics and Adsorption. By now, the reader (if he has followed up to this point) will silently complete the title into something like: Electron Transfer Coupled to Homogeneous Reactions and Adsorption. The notation of

reaction sequences in the EC nomenclature is properly introduced. Instead of providing a generous overview, the authors limit themselves to just four examples, and one (EC_2) is already a subspecies of another one, and the first one is the simple electron transfer. The second example is a two-electron transfer. Hardly a good idea because the authors must have been aware of the debates about the question for a real simultaneous transfer of two electrons (or two subsequent ones). The reviewer is sure to remember textbook examples of EC mechanisms without these complications. Perhaps the authors shared this feeling—after a brief detour into Fick's second law modified to take into account chemical reactions the certainly needed discussion of the EC-mechanism is reduced to a one-electron transfer (p. 236). Somehow, in the example, no equilibrium between the electrooxidation product and the product of its chemical conversion was assumed. Detailed mathematic treatment proceeds, and suddenly, symbols Λ and K_1 are introduced. At first glance, some symbols seem to be coupled in an arbitrary manner, but quite a few pages down the road, the patient reader (by now certainly not surprised anymore by this mode of presentation) learns, that Λ is a dimensionless heterogeneous rate constant and, K_1, a dimensionless homogeneous rate constant. Fortunately, most authors stick to the old fashioned approach of introducing a symbol properly when used first. The plot most readers might have been waiting for showing CVs at various scan rates and rates of the following chemical reaction appears finally on p. 238. The figure caption is mysterious at best: (a)=$K_1=10^1$ is a mild example. Multiplying the values at both axis by −1 seems to be a habit of the authors, although a rather superfluous one. The reviewer certainly respects the authors' intention to demonstrate the close interplay between scan rate and chemical reaction rate, but in this form, it is just "overcondensed." The heterogeneous rate constant is a large one in this first case (although the reader wonders why it must be exactly 1.973 cm^{-1} and not—just perhaps—2 cm^{-1}. The second case evaluates the influence of this rate constant, now set to a much smaller value: 1.973×10^{-4} cm^{-1}. The following discussion of two examples of the EC_2 mechanism is less mathematical and more chemical. Mercifully, the example shown at the start of the chapter is not pursued further. Now, the flood of figures overwhelms the authors. Plots still dealing with 2,6-diphenyl-pyrylium are mixed up with equations containing fumarate and maleate. Perhaps this is the reason the reviewer was lost on p. 253: "However, at 10 Vs^{-1} (C).." left him puzzled. After some page turning, he found a figure on the following page containing indeed a trace simulated at this scan rate—but it was labeled (c). Continuing to the ECE-case will certainly make matters more complicated. There is indeed no disappointment in stock. Figures are still dealing with DEM (this is the maleate case), the text has moved on. Again, the authors do not pursue the initial example further—and the reader wonders again: why? Because of the numerous possibilities of changing parameters and their influence, a descriptive approach (keep all variables fixed except for one) is fine, even finer would have been an approach where the reader does not have to search for this varied parameter. Subchapter 7.8 starts with a surprise: Its title is: ECE vs DISP: Presumably, the reviewer lacks the particular type of humor of the authors. DISP refers to the very special situation, where the product of the first electron transfer reaction reacts with the product of the chemical follow-up reaction yielding the starting material and the final product of the ECE-sequence:

$$A + e \rightleftarrows B$$
$$B \rightleftarrows C$$
$$C + e \rightleftarrows Z$$
$$B + C \rightleftarrows A + Z$$
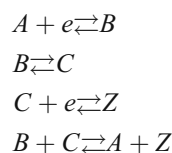
The discussion of examples nicely illustrates the general importance of this very specific problem in an introductory textbook: The only experimental illustration the authors managed to find is a plot of data from chronoamperometry. The influence of a chemical reaction preceding the charge transfer (CE-case) is certainly more frequent. Certainly, temperature has an effect on the rate of the chemical reaction. The scan rate will also be of importance. In Fig. 7.22, this should be evident, but somehow, the authors manage disaster. The scan rate must be coded mysteriously in symbols like 100 min/s and given the dedication to multiply almost everything by −1, the code +47° presumably means −47 °C. But—who knows? Perhaps the sudden disappearance of three nitrogen atoms from the 1,2,3-trimethylhexahydropyridazine on p. 267 is somehow related?

Finally, the case of adsorbed reactants and products and the influence of adsorption in general is considered. The reader will find the expected CVs with potentials of oxidation and reduction peaks being equal after a while and after being surprised by quite-different-looking CVs. No problem, they are leftovers from the previous section. Finally, some remarks are devoted to CVs obtained with insoluble particles and droplets of immiscible liquids attached to an electrode surface.

Cyclic voltammetry may be applied in combination with electrodes and solution beyond the stationary or stagnant case. Controlled convection as generated at a rotating disk electrode, in a channel electrode or in turbulent pipe flow are popular examples. Further modes of enhanced transport like bubbling inert gas or application of ultrasound (presumably the authors had this or sonication in mind when rambling about insonation—a word unknown in

major dictionaries) may also merit attention. The former approach has gained importance in kinetic studies because the transport can be calculated precisely. There are several textbook and review chapters in monographs available—plenty of material to compile a short description of the matter. Instead, the authors dwell on Osborne Reynolds because they feel a need to tackle the details of turbulent and laminar flow. Perhaps, as some sort of compensation, no proper example is provided demonstrating the capabilities of the rotating disc electrode (the ring-disk-electrode is not mentioned at all, but this is certainly another story). The section on the channel electrode starts with the both intriguing and mysterious sequence: "In the channel, electrode, solution.." It deals with laminar flow, the case of the turbulent pipe flow as studied decades ago very successfully somehow escaped the present authors' attention. Instead, the authors discuss chronoamperometry at channel electrodes. Apparently, the criteria applied to subjects included and excluded have escaped the reviewer—more on this below. At least the authors include the possibility of a channel electrode operated with an electrolyte solution at 500 atmospheres. In a somewhat confused discussion, switching between laminar and turbulent flow, the former wins—the advantages of turbulent flow are flatly overlooked (they have been discussed extensively in several reports in the late 1970s and early 1980s). The use of ultrasound is a different matter. The essence of a somewhat long and winding story seems to be twofold: Transport is enhanced, and anything sticking to the electrode is effectively removed.

The final chapter on voltammetry in electroanalysis is a mixed bag. Step and pulse methods are treated briefly, stripping voltammetry is discussed, the domestic US legislation related to mercury is presented excessively (including an impressive picture of a warning sign suggesting limited consumption of a certain fish taking into account gender, age, and pregnancy), and ultrasound is used once more.

The appendix provides some glimpses at the mathematics of numerical simulation of cyclic voltammograms.

The index might provide some help—but an entry "working electrode" with exactly one reference to one page in such a book leaves the reader with some doubt about the reliability of this index.

The text appears to be written in a somewhat sloppy manner, even the non-native speaker will frequently wonder about gross typing errors (the word "experientally" on p. 28 is simply nonexistent, the term bloke on p. 207 is hardly a compliment to any male reader) or sentences floating away unfinished lacking logic, etc. (e.g., on p. 9, middle, p. 188 bottom). Figures are numerous and helpful; apparently, the designer had a rather strange feeling of reasonable sizes and proportions. Many figures (e.g., on p. 234 and 235) are drawn rather careless—they look simply ugly. The device depicted in Fig. 1.14 will flatly refuse to work—a switch is missing. Current densities are associated with the symbol j according to IUPAC's suggestion, and not IA^{-1} as shown in Fig. 3.9. j is used to denote a flux of particles instead. The reader should be careful nevertheless: this symbol is used in Fig. 3.12 (ii) as a label of the current axis with the unit mol cm^2 s^{-1}—whatever this means. The book does not contain a list of symbols and acronyms (standard in textbooks the reviewer dares to claim); thus, the authors might simply have overlooked this aberration. Figure 5.3 contains a gross error: the label on the right-hand side must be $\sqrt{D\pi t} >> r_e$ as stated in the following text correctly. Summing it up—the buyer of this book, expecting a helpful, well-organized introduction into a frequently used, almost omnipresent method will be severely disappointed. Instead, he obtains one of those numerous examples published with growing frequency where an author glues together his very personal perspective of life and science. With some searching, many questions will be answered somehow—but not in a systematic manner and certainly not in a way helpful as guidance for the novice. A missed chance.