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BOOK REVIEW

Rudolf Holze

R.C. Alkire and D.M. Kolb (eds): Advances in electrochemical science and engineering, vol. 8, Wiley-VCH, Weinheim, 2003, 378 p., 159€; ISBN 3-527-30211-5

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As the most recent volume of a successful series established by the present editors in 1990 in continuation of an equally successful enterprise started initially in 1961 edited by P. Delahay and C.W. Tobias, this book contains four reviews of very different topics in current electrochemistry.

J. Fleig reports on the use of microelectrodes in solid state ionics in the first chapter. Electrochemistry at/with solid electrolytes (which are invariably exclusive or at least predominant ionic conductors) is a popular subject of research especially for sensor and high-temperature fuel cell researcher. The use of microelectrodes is certainly an attractive approach to reduce sample size, and amount of material needed; combinatorial chemistry is an additional argument. On top of this electrode, materials (active masses) as employed in e.g. lithium ion batteries have turned out to be more than just redox-active matter; according to their behavior they are also complicated electron-ion conductors. Before actually reviewing recent advances in solid state ionics achieved with microelectrodes the fundamentals of ionic conductors are described with particular attention to analogies with liquid-solution electrochemistry. Not surprisingly impedance measurements (once again somewhat erroneously called impedance spectroscopy) are treated extensively. The need for microelectrode experiments follows quite logically from the experimentally observed inhomogeneities (grain boundaries, defects, polycrystallinity) of real samples. Practical as well as theoretical aspects of microelectrodes are treated. Numerous examples of studied materials and the interpretation of the observed data conclude this chapter.

Nonlinear dynamics observed in electrochemical systems are treated by K. Krischer. Beyond oscillating reactions treated as examples in student lab courses and complicated phenomena associated with corrosion and passivation more recently in numerous other areas, nonlinear potential-current relationships (e.g. in several fuel cell electrode reactions) have been observed. Beyond these still rather popular or obvious examples of nonlinear relationships, self-organization has become increasingly well known. The present chapter treats these phenomena in a very general, systematic and fundamental fashion. The rather complicated coupling between numerous electrochemical variables including the external circuitry (potentiostat, wiring) is considered. From the point of view of an experimentalist who wants to get rid of oscillations most likely caused by electronic insufficiencies of the potentiostat, the wiring or the reference electrode, this chapter is only of limited help because this very practical trouble-shooting aspect is buried in the fundamental general approach. A few figures show errors which obviously escaped the author's attention: in Fig. 44a the pictured circuit is short-circuited, in Fig. 45a a strange arrow survived editing.

The growing availability of highly doped (and correspondingly conductive) diamond films suitable as electrodes for all kinds of electrochemical investigations together with the prospect of an extremely stable electrode material has stimulated the use of these electrode materials. Somewhat unfortunately, reviews on the electrochemistry of diamond have appeared already recently (see e.g.: R. Tenne and C. Levy-Clement, *Isr. J. Chem.* 38 (1998) 57; M. Hupert, A. Muck, R. Wang, J. Stotter, Z. Cvackova, S. Haymond, Y. Show and G.M. Swain, *Diam. Relat. Mater.* 12 (2003) 1940; or even by the author of the present chapter himself: Yu.V. Pleskov, *Russian J. Electrochem.* 38 (2002) 1275). In addition the rather long production time renders any review in this field rather fast as being out-of-date. Yu.V. Pleskov covers recent advances up to the year 2000. In the brief introduction the obvious and frequently quoted facts (mentioned above already) are repeated. The preparation of thin films of diamond predominantly by chemical vapor deposition is described with particular attention to boron doping.

R. Holze
Institut fuer Chemie, Technische Universitaet Chemnitz, 09107 Chemnitz, Germany
E-mail: rudolf.holze@chemie.tu-chemnitz.de

Crystal structure and morphology as studied in particular with Raman spectroscopy and electrophysical characteristics (i.e. conductance) are briefly discussed in the following section. Any relationship to the electrochemical behavior remains unclear. The first truly electrochemical data are cyclic voltammograms of diamond of various qualities recorded in acidic electrolyte solutions. They nicely demonstrate (by direct comparison with also reproduced CVs of platinum and highly oriented pyrolytic graphite) the extremely wide electrochemical window making diamond such an attractive electrode material. Corrosion resistance and electrochemical etching are further topics in this chapter, which deals for reasons unknown to the reviewer with the preliminary characterization only. The properties of semiconducting (i.e. slightly doped) diamond and the electrochemical double layer established at this material as studied in particular with impedance methods are the subjects of the following chapter. Electrode kinetics of numerous inner- and outer-sphere reactions are treated extensively (although certainly not exhaustively) with respect to the conductivity (i.e. the semiconductor semimetal nature) of the employed diamond. Because of the semiconducting nature of slightly doped diamond photoelectrochemistry can be employed for diamond characterization as reviewed in a brief chapter. In a final two-page chapter electrochemical and photoelectrochemical characterization of diamond are treated. Actually only a list of already mentioned methods and further variations of methods already discussed in the previous chapter are presented. This chapter should have been merged into the proper place. The figures are of a quality below standard in quite a few times, this should not have happened in a series of this standard (and price). Table 1 is an illuminating result of an essentially needless attempt to tabulate everything. HTHP diamond is initially not explained, in the latter text an explanation is hidden, and the only reason to include this material is a minute deviation in refractive index from that of cubic natural diamond. The inclusion of epitaxial diamond films, which show only a slightly larger deviation in refractive index seems to be justified by a minute difference in lattice parameter. Once again this is nowhere discussed or even mentioned in the text, thus the table might have been omitted. The somewhat arbitrary arrangement of material lacking logic and economy seems to be a general feature of this review. This chapter might be useful for those without access to the journals mentioned above or preferring an English-written article; otherwise this chapter might have been written better a few years later providing a desirable update.

H.-H. Strehblow reviews both experimental aspects and fundamental concepts of passivation and the subsequently established passivity of metals in the final contribution in this volume. There have been whole books and series devoted to the passivity of metals, thus the author should provide strong arguments for offering a further installment on this subject. The editors introduction leaves the question open: a review of experimental methods and theoretical concepts is offered. After a somewhat historically colored introduction, the author describes aim and purpose: to show that a careful combination of electrochemical and spectroscopic (this may well include surface-analytical methods as well) tools is the best way to a better and reliable understanding of passivity and related phenomena and processes. After a brief and summary treatment of the thermodynamics of passivation, the kinetics of electrode processes at passivated surfaces are discussed with respect to formation and behavior of passivation layers. Experimental methods particularly suitable for passivation studies are briefly reviewed in the next chapter. Whereas the electrochemical methods are boiled down to split-ring disc electrodes (and the corresponding need for a tripotentiostat) and hydrodynamic modulation (in particular square wave modulation) of the rate of rotation of this electrode assemblies, the surface analytical tools are somewhat surprisingly and certainly no more up-to-date and are limited to ex situ electron spectroscopies. Somewhat arbitrary acronyms assigned to the few methods are listed incompletely only in the corresponding section at the beginning of this chapter. The selection of methods comes as no surprise when looking at the major scientific areas of activity of the author, but this limitation looks somewhat strange when considering the much broader claim in the authors introduction and when considering the state of the art already established for quite a few years.

In subsequent chapters the chemical composition of passive layers on pure metals and their alloys as deduced from measurements with these ex situ methods and their electronic properties are described. Structural details as revealed with diffraction and absorption methods employing X-rays (these methods were somewhat arbitrarily overlooked in the chapter on methods) are discussed in a separate chapter. Implications for the general and unambiguous understanding of passivity are somewhat hard to find. Chances to illustrate a point by describing a figure adequately are sometimes missed—Fig. 54b can be understood properly only after extensive consultation of a larger part of the accompanying text. Although somewhat unexpectedly scanning probe methods are introduced, selected results illustrate surface reconstruction (hardly related to passivity) and formation of oxide layers—the initiation of passive layer buildup. Only briefly—on about a page—the breakdown of passivity in the presence of aggressive anions is discussed. The final sentence of the concluding remarks sums up the situation nicely: Surface science applied to corrosion phenomena is promising for future research. The present review provides only a narrow glimpse at this bright horizon. Another conclusion: When looking at the list of references the number of quoted contributions from the present authors easily dominates—consequently this resembles the personal review of own contributions to an already well-treaded area of research; not exactly the review most readers might have expected.

The book is fairly carefully prepared, unfortunately quite a few figures presumably converted with inadequate means are of rather poor and, in some cases, almost illegible quality. The editors as well as the contributing authors should resist to the temptation to simply convert figures via software without looking carefully at the finally obtained quality. Despite this weaknesses the book is a must for all libraries already owning previous volumes, in addition the contributions on the four treated topics themselves (with the conceivable exception of the chapter on diamonds—this topic has been the subject of numerous reviews recently) justify acquisition for those entering these fields.