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## Piero Zanello: Inorganic electrochemistry: theory, practice and applications

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In a most recent special issue of the *Journal of Solid State Electrochemistry* selected contributions of the third Chianti Electrochemistry Meeting on Metal-containing Molecules (July 2004) have been published. They deal—as suggested by the title—predominantly with electrochemical investigations of organometallic and related compounds thus providing an up-to-date picture of current inorganic electrochemistry. It certainly comes as no surprise that the organizer of this meeting is the author of the extended textbook reviewed here. The importance and value of electrochemical and more recently spectroelectrochemical methods in experimental inorganic chemistry (and also in organic chemistry, sometimes these areas are hard to separate) can hardly be overestimated. This is in strong disagreement with the treatment of even the most basic electrochemical methods of investigation (perhaps excluding the various pH-electrodes because of the pH-dependent equilibria established at the solution/solid interface related to the establishment of the measured electrode potential). The short shrift given to these methods extends well into the published literature. As nicely stated by P. Zanello many publications on inorganic topics contain a few experimental data (e.g. some cyclic voltamogram) suggesting that everything necessary has been done to characterize the compound under investigation completely from the electrochemists point of view. In many cases this suggestion collapses at even the most superficial inspection of the presented results. Sometimes strange (or simply arbitrarily or convenient) reference electrodes are used making comparison with data published elsewhere (and perhaps obtained using standard references or being carefully converted to standard potential scales) impossible. Cyclic voltamograms have

been measured in arbitrary ways without considering suitable starting potentials, scan directions and potential limits, not to talk of different scan rates. From the inorganic chemists point of view these complaints might look overdone, but whenever a discussion between electrochemists and inorganic chemists about the meaning of the results supplied by the latter gets serious the lack in careful planning and execution of electrochemical experiments tend to show up.

The textbook prepared by P. Zanello provides a promising attempt to remedy these maladies. In a book of impressive scope and size three major parts of very different length are collected. In a first theoretical part fundamentals of electrode reactions and of voltammetric techniques are treated extensively always having in mind the intended reader. Thus some forms of displaying relationships and using terminology may be somewhat unfamiliar to the electrochemical specialist, they nevertheless will hopefully be helpful in transmitting the information to the non-electrochemist. The limitation to traditional electrochemical methods may look somewhat arbitrary, inspection of inorganic chemistry journal reveals, that still these techniques are most popular in this community, presumably because the methods can be applied rather straightforwardly at modest costs. Practical aspects are treated in a short, but nevertheless very helpful chapter. Unfortunately the author seems to limit the descriptions mostly on own, very personal experiences. Beyond any doubt aqueous calomel and silver chloride reference electrodes are very suitable for those working with aqueous electrolyte solutions. The need for salt bridges is certainly a drawback when using these electrode with nonaqueous solutions. For these solutions various other reference electrodes have been described—and even nonaqueous versions of said electrodes of the second kind have been described (including their practical limits: G. Gritzner and J. Kuta, *Pure Appl. Chem.* **56** (1984) 461). In any case—in this chapter dealing with both aqueous and nonaqueous solutions in

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every case the nature of the solution should have been stated more clearly leaving the reader not alone with his doubts. Somewhat surprisingly this chapter does not contain any reference to instrumentation beyond electrodes, solutions and glassware. Although it may be a valid point to consider discussion of particular potentiostats and other instruments as being useless for such a textbook some general information about the need of e.g. a high voltage available at the counter electrode to maintain proper potential control even in poorly conducting solutions might have been helpful. In any case a simple power supply (constant voltage source) as depicted on p. 20 should certainly not be called a potentiostat—this is plainly confusing. The rest of the depicted circuit diagram will only increase uncertainty in the nonexpert reader.

The bulk of the book—444 pages—is devoted to an extensive review of the electrochemistry of inorganic compounds of all types. The majority of the treated compounds are metal complexes and organometal molecules, but high temperature superconductors are considered also. The electrochemistry of other compounds—like e.g. metal oxides in unusual states of oxidation or of molecular compounds - is not treated, perhaps these subjects are of only minor interest to the current inorganic chemists community. Although missing is any description—even a minor reference—to the use of numerical simulation. Certainly only a minority of inorganic chemists will be interested in kinetic data most easily extracted from cyclic voltammograms with the help of any of the currently available software packages; but the comparison of measured voltamo-

grams with calculated ones using various mechanisms, rates of electron transfer and chemical reaction, diffusion coefficients etc. will be most helpful when interpreting complicated results.

The book provides a wealth of information, which can be accessed easily via the extensive subject index. It contains numerous figures. Although the reviewer will fully accept the convention, that pictures just used to illustrate e.g. a minor practical aspect may be of basic quality only numerous figures in the book are somewhat too far away from today standards. Because the book will hopefully be used by many students entering this field they provide misleading examples. These arguments should not discourage any potential reader (and buyer) of this book, which will be most helpful when entering the area of electrochemistry from the inorganic chemists field. Somewhat unfortunately another, more serious limitation lingers in the mind of the reviewer—and perhaps also of a reader, who is already more familiar with electrochemistry: The limitation of both the theoretical and the practical section to a very small selection of techniques is not appropriate anymore. As could be seen in some publications in the past and can be seen in the current literature with increasing frequency advanced electrochemical as well as spectroelectrochemical techniques have opened up new avenues towards scientific discovery which should be made available to the general chemical audience. Perhaps the author plans a second edition or extended version of this most promising book. Consideration of joining with an experimental electrochemist covering the gaps indicated above will elevate this book to an even higher level.