

Impedance spectroscopy [E. Barsoukov and J.R. Macdonald (Eds.)]

WILEY-INTERSCIENCE, Chichester, 2005, 595 + XVII p., 77.95 £; ISBN 0-471-64749-7

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Published online: 28 February 2007
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Of all electrochemical methods, the measurement of the impedance of an electrochemical cell or of an electrode (which is frequently and somewhat misleadingly called impedance spectroscopy) is most likely the most powerful and versatile one. The still growing number of available instruments and software programs needed to run the instruments and to evaluate the obtained data has greatly enlarged the community of researchers applying this method. The seemingly easy use of instruments and data processing is in disconcerting contrast with the complexity of the obtained data and the variety of procedures available for evaluation. Thus, an up-to-date textbook aimed at researchers in particular at the M.Sc. and PhD levels considering the use of this method or a specific variation of it is certainly a helpful addition. The book reviewed here has been published in its first edition 1987, and although its focus was on solid electrolytes, the width of contributions [ten authors were initially involved, but a remarkable (and remarkably successful) effort was made to produce a uniform work without undue repetition or overlap] provided helpful information even to those researchers not dealing with this particular family of materials requiring rather different experimental setups as compared to impedance measurements with electrodes in contact with solvent-based electrolyte systems. The present, significantly enlarged second edition has broadened the scope together with the addition of a second editor. Several completely new sections deal with batteries, fuel cells, porous electrodes, and photochromic materials.

In the first chapter, fundamentals of impedance measurements are described; some historical background is provided.

Attention is paid to the evaluation of data. The still very popular concept of equivalent circuits is introduced stepwise. Finally, two fairly “well-behaved” systems with aqueous electrolyte solutions are discussed in detail. The examples are somewhat dated—they rely on results published in 1960—and they may be somewhat misleading for the novice. It may be justified to qualify a reaction as diffusion-controlled when the charge transfer is very fast, but such a distinction is always arbitrary. Because of experimental limitations (as somewhat wittingly discussed in the book and attributed to the historical context of the quoted primary source), the upper frequency limit is 20 kHz, and consequently, the displayed data do not show the high-frequency loop associated with the double layer capacitance (which is certainly present) and the charge transfer resistance. It is a somewhat unusual approach to make a reader and researcher familiar with a modern method and its capabilities. A third example deals with a complete solid-state cell. The result looks almost simple, and the explanation is short. Upon careful reading, it becomes obvious that simplicity is obtained only by invoking numerous results obtained with other methods. Nice proof of the frequently uttered (and almost as frequently unfulfilled) request for independent support of impedance measurements with as many other electrochemical methods as possible! Whether it is a convincing introductory example seems to be a different question.

The second chapter, simply called “Theory,” deals with chemical and physical processes and their electrical analogs without any obvious systematic approach. On p. 80—at the end of this part of the book, which the authors now call section (and to illustrate this a lengthy declaration of copyright is inserted here)—the reader feels that an attempt has been made to introduce the most important elements of equivalent circuits as used in the evaluation of impedance measurements. The subsequent section deals with modeling

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of electrochemical systems with equivalent circuits based on the considerations and elements of the preceding section. The authors' intention calling this section "Physical and Electrochemical Methods," although only electrochemical systems are treated, remains an open question. Terminology is sometimes almost philosophical: The difference between supported and unsupported situations (these are indeed the terms used in the table of contents) can be identified only after some reading; the former term refers to an electrolyte solution containing a supporting electrolyte, while the latter refers (again) to solid electrolytes where the situation is entirely different.

Chapter three is devoted to measuring techniques and data analysis—both subjects are requiring attention because in both areas, considerable errors can be made even unintentionally. First, measurement techniques are discussed. Somewhat astonishingly, much space is devoted to modified Wheatstone or Berberian–Cole bridges and Lissajous figures, and only at the very end frequency response analyzers FRA are mentioned with a big caveat related to the possibility that an FRA may generate data even when not connected to the electrochemical system under investigation. Price is mentioned as a problem. The quotation is of 1986—this is presumably the date this section was finished. It may be considered as a nice historical review, but a novice in the field would certainly appreciate a more up-to-date treatment. The following section on commercially available systems is closer to this aim. Valuable hints for experimental work (including studies of bulk material properties of, e.g., solid electrolytes) can be found. Finally, data analysis is treated. Because the book is limited to the equivalent circuit approach—this has been subject to criticism in the past, the use of transfer functions (which are unfortunately much more abstract and thus somewhat more difficult to handle) is mentioned briefly in passing in the section on corrosion (p. 343)—analysis boils down to the proper mathematics (nonlinear least square fit) needed to get the values of the parameters assigned to the components of the equivalent circuit. The example finally discussed is rather theoretical (it is a network of passive electronic capacitive and Ohmic components); certainly, some real-world electrochemical examples preferably with properties possibly resulting in ambiguous equivalent circuits may be more helpful. A list of available software packages (even though such a list has only a very short half-life) perhaps with some evaluating remarks might have been a good addition. Instead, three-dimensional plotting of impedance data seems to be a specialty of the author (one of the editors), a cursory glance at the current literature suggests that two-dimensional plots are still considered sufficient in most cases. Perhaps that is the reason this chapter seems to be updated from the first version only to a very limited extent.

On the remaining 400 pages in chapter four applications of impedance measurements are described. At this point, the reader may have realized that solid electrolytes are a dominating feature of this book, and he may have noted also that typical features of an introductory textbook (one of the claims in the preface) like, e.g., equal coverage of all typical applications, a systematic description keeping personal preferences at bay or selection of both illuminating and real-life examples are not a strong side of this book. The first section deals with characterization of materials (i.e., solid electrolytes), a short contribution on immittance measurements at high resistivity ionic and dielectric materials follows. Complete solid state devices (sensors, solar cells) are handled in the next section. Corrosion studies with impedance measurements—certainly a most prominent field of application—are covered extensively in a further section. It includes numerous examples as well as descriptions of some variations of impedance methods. Electrochemical power sources (presumably more precisely called electrochemical energy conversion and storage devices) are covered in the final section. After some general remarks pertaining to specific problems related to the impedance of complete systems (i.e., cells, batteries etc.), primary and secondary cells are treated in a subsection on batteries, supercapacitors and porous electrodes follow, and fuel cells ranging from ambient temperature alkaline to solid oxide fuel cells are dealt with in the final part. Although not exhaustive, helpful examples of successful applications are provided encouraging further application of impedance measurements.

The book is fairly well written, and in most parts easy to read and richly illustrated. Some illustrations seem to be somewhat dated and almost hand-drawn; this does not interfere substantially with their purpose. Even confusion of the x - and y -axis (see, e.g., p. 458 or 460) causes only momentary irritation. Sometimes, terminology is strange—an irreversible interface can be imagined only with some guesswork, and it is rather mysterious why corrosion studies have long time constants. A frequency region of 10^{-3} – 110^{-4} Hz (p. 343) is most likely only an amusing printing mistake, but perhaps it is again a hidden indicator; these frequencies are certainly not the lower limit with modern instruments, but since most references in the respective section date from the years of the publication of the first edition, this section may be somewhat dated also, like some other, too. Authorship of the various chapters, sections, and subsections is not always unequivocally established, and perhaps the sheer number has contributed to some repetition of, e.g., experimental details. The organization of the list of references is quite unusual—finding a reference may turn out to be a cumbersome business in the single list at the end of the book, which in addition contains a few mix-ups. A brief and unfortunately

incomplete list of abbreviations follows (the acronym RMA remains unresolved as well as the description “CT specimen” on p. 426). Despite the considerably broadened selection of authors and examples of applications, the book remains closely attached to impedance measurements with solid electrolytes—thus somewhat less useful for most other

electrochemists. It is nevertheless a must for all libraries associated with educational and research institutions dealing with electrochemistry; the price makes it accessible even for the personal library of a researcher. One purpose stated in the preface—M.Sc. and PhD students will be the major benefactors of this book—is unfortunately hardly met.