

Book reviews

Solid Polymer Electrolytes, Fiona M. Gray

x + 245 pp, VCH Publishers, New York, 1991,
DM 128.00, ISBN 0-89573-772-8

Electrochemists talking about solid polymer electrolytes in modern systems of electrochemical energy conversion or storage most often refer to perfluorinated ion exchange membranes used with great success in electrolyzers, fuel cells and systems for electrosynthesis. Nevertheless a wide field of polymers mostly based on polyethers also belongs correctly to this type of electrolyte. These materials, first mentioned with respect to potential applications in electrochemistry in 1973 and suggested as possible components in electrochemical energy storage systems in 1978, are the subject of this book.

Starting with an overview of polymer electrolyte-based devices (mainly batteries and electrochromic systems) the book covers all relevant aspects of polymer electrolyte materials. Focusing on oxygen-containing poly-ethylene and poly-propylene oxides (poly(ethylene imines) and thiaalkanes are mentioned briefly) the general properties of the polymers, their interaction with a variety of salts, the structure and morphology and aspects of the conductivity of polymer-salt electrolytes are reviewed. Considering the fact that high molecular weight poly-ethylene oxide is a poor material itself (up to this point on page 95 the reader may have shared the author's seemingly optimistic attitude with respect to the marvellous conductive properties of this material), possible modifications of the polymers, as described in the initial chapters by introducing modifications of the polymer structure are evaluated. This should result in improved mechanical properties relevant for practical applications, and in better conductivities. Further developments of polymer electrolytes including proton conductors, organic-ceramic hybrid materials and polymer salts with multi-valent cations are discussed in detail. Transport properties of polymers electrolytes as viewed from a macroscopic as well as a microscopic point of view are discussed; experimental techniques used in the investigation of these properties are described briefly. Attention is paid in particular to ionic species present in the polymer electrolyte and their mobility. The electrode-electrolyte interface is reviewed in the final chapter; the discussion is focused on the lithium-polymer interface, which has been studied preferably so far, because of the practical implications in secondary lithium batteries. A somewhat selective index concludes the book.

The reader will be impressed by the amount of literature collected and reviewed in this book. Unfortunately quite a number of confusing statements and explanations will disturb him. The arrange-

ment of the various chapters contributes to a perplexing impression. Some examples will explain this. Solid polymer electrolyte is a label also generally attached to ion exchange membranes; the acronym SPE has even been protected as a trademark. Whereas ion exchange polymers are not even mentioned in the text or the index, the reader is left waiting for a definition of solid polymer electrolyte differing from this well established meaning. It is never clearly stated, but finally it can be assumed, that the author may have defined it like 'a quasi-solvated salt in a solvating (coordinating) polymer'. Instead of starting with a clear definition of the system to be reviewed and discussed, the author presents probably the most impressive application of polymer electrolytes in secondary batteries in the initial chapter. This might have been a fine introduction — but already on page 6 the reader stumbles on the statement that even theoretical energy densities of polymer electrolyte batteries are no match for commercially available cells (whatever a MoliCell mentioned for the comparison may be). Fortunately, this disappointment is corrected a few lines later, when systems with indeed promising data are described. Unfortunately, the reader still does not know clearly the operating conditions. Initially operating temperatures well above room temperature were indicated, but at the end of the first chapter the range of operating temperatures is between -10°C and 130°C . This way of confusing the reader by giving contradicting or incomplete information is one of the less attractive features of this book. Many examples can be marshalled in order to support this statement. Certainly some of them are caused only by sloppy writing. On page 10 a mysterious loss of 10% of the structure of the cell voltage curve is stated; on page 20 the required lifetime of a practical battery should be more than two days; in Fig. 1.4 the curves were surely recorded at different current densities rather than capacities, on page 22, ITO is presumably indium tin oxide and in Fig. 10.3 the axes are probably inverted. In addition, numerous incomplete figure captions, omitting essential information and sometimes containing serious contradictions between the figures, their captions and the explanations given in the text, leave the reader wondering. This is a particularly annoying impression in those sections dealing with ac impedance measurements (presumably the same as ac spectroscopy as stated on page 216). The equivalent circuit as outlined in Fig. 9.8 and labelled in the caption is discussed in surprisingly differing terms in the text. Fig. 10.12 is even worse. The equivalent circuit and impedance plot imply that no current will ever pass this interface. Perhaps this is correct, because this circuit may refer to an interface blocked in the absence of a dc current with

an extremely poorly conducting interphase. As no information with respect to this experimental condition is given, the reader is again left wondering. In all cases of displayed impedance plots, no attempt is reported of fitting the equivalent circuit parameters towards the measured data and checking these parameters versus the properties of the components present in the electrochemical cell. This greatly diminishes the value of these plots and certainly does not contribute to a good standing of electrochemical impedance measurements as an experimental method.

The formation of poorly conducting layers at interfaces between, e.g., lithium and various electrolyte materials including polymeric ones, is of tremendous importance for practical applications. The voltage delay observed during the discharge of almost all lithium batteries is one consequence. No discharge curve showing this detail can be found in the book, and surprisingly this feature is introduced only in the final chapter. Certainly the author is an expert on this type of electrolyte, but unfortunately the book supports this statement in an undesirable way: the author's point of view is in the middle of this field, and she may, perhaps to some extent, have lost the sense of perspective necessary for a good overview.

For a reader already somewhat familiar with solid polymer electrolytes as defined above, this book provides a wealth of information on many aspects of these fascinating materials. The haphazard arrangement and the numerous confusing or simply wrong details will not distract him. For the novice it will be an unnecessarily difficult task to get a clear picture of solid polymer electrolytes from this book, consequently this book can be recommended for libraries only.

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**Advances in Electrochemical Science and Engineering,
Volume 2**

Edited by Heinz Gerischer and Charles W. Tobias

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This volume is well presented, with clear text and figures, and few typographical errors. It contains four chapters, two addressing topics of technological importance – electrocatalysis of hydrogen evolution, and solid oxide fuel cells, and two concerning novel experimental techniques for the study of electrode surfaces and reaction kinetics – namely second harmonic generation as an *in situ* probe of single crystal surfaces, and flow modulation techniques in electrochemistry.

S. Trasatti presents a thorough review of hydrogen evolution electrocatalysis, and provides a useful survey of the state of the art in hydrogen cathode research and applications. The chapter links theory and practice, providing a discussion of the concepts

underlying electrocatalysis, as well as reviewing the performance of a wide range of catalytic materials.

A. Hammou discusses the thermodynamics, rate processes, materials, and technology behind solid oxide fuel cells. The broad nature of this topic renders thorough review difficult, but a useful overview is provided. One omission is the absence of discussion of the planar SOFC designs which are currently the subject of much industrial interest – this serves to unbalance the cell design and performance of the chapter.

G. L. Richmond outlines the extensive advances made in surface second harmonic generation in the past decade, with particular emphasis on its application to metals in an electrochemical environment. This technique yields information on the structural and electronic properties of electrode surfaces, and the advantages and limitations of the technique are discussed.

Finally, a review of flow modulation techniques in electrochemistry is provided by C. Deslouis and B. Tribollet. A thorough discussion of the theory underlying the electrohydrodynamic (EHD) impedance technique is given, showing that information on mass transport and electrode processes can be obtained. Some applications of the technique in areas such as corrosion and electrocrystallisation are also provided.

Overall, the volume is well presented and well written, and can be recommended.

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Electrochemistry in Colloids and Dispersions

Edited by Raymond A. Mackay & John Texter

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This book is a compilation of the papers presented at the Symposium on Electrochemistry in Microheterogeneous Fluids held at the New York Waldorf-Astoria during August 1991. The contributors count among their number several of the leading lights in the fields of colloid and electrochemistry, including (in no particular order) Grätzel, Serpone, Osteryoung, Mills, Fox and Pelizzetti, giving the book a very authoritative feel. In fact, it fully lives up to the claim, made on the back cover and in Raymond Mackay's preface, of being the first publication to truly comprehensively treat the merging of colloid science and redox electrochemistry. There are thirty six chapters, including both original research contributions and in-depth review articles, supplemented by an exhaustive 36 page index enabling the rapid location of required subjects of interest. Unusually for a multi-author publication, the style of presentation is of a uniformly high quality throughout, reflecting the thoughtful job performed by the editors in the organization of the text.

The articles are divided into five main sections:

Electroanalytical Methods and Applications, Solute Distribution, Diffusion and Transport, Polymers and Latexes, Electrosynthesis and Electrocatalysis and Colloidal Metals and Semiconductors. John Texter introduces the proceedings with an excellent, if uncritical, review that serves as a general survey of the areas of coalescence between colloid science and electrochemistry, a summary of the majority of the material within the book and an explanation of the way in which the subject matter has been divided and ordered.

Section one, Electroanalytical Methods and Applications, contains five papers all of which discuss the applications of voltammetry to surfactant / micelle based systems and vice versa; for example, Fiscaro *et al* use quinones in anionic micelles as models for biological membrane electron transfer processes whilst Franklin *et al* employ cationic surfactants to extend the analytical utility of oxidative voltammetry by the expansion of the solvent window.

Section two, Solute Distribution, Diffusion and Transport, mostly examines the role of surfactants and micelles in transport of electrochemically active species to the electrode surface. Texter here contributes an interesting paper modelling the behaviour of electroactive probes in emulsions and micellar solutions during rotating disc voltammetry experiments. Other noteworthy papers are those of Medina *et al*, studying redox-switched vesicle formation, and Cannon *et al*, determining micellar diffusion coefficients by electrochemical and luminescence quenching techniques.

Sections three and four, Polymers and Latexes and Electrosynthesis and Electrocatalysis, respectively, are the two shortest sections in the book and involve themselves for the most part with voltammetry of conducting polymers and the applications of surfactant

systems to the modification of electrochemical reaction mechanisms facilitating the opening of new electrosynthetic pathways.

Section five, by far the largest, concerns itself with the matter of colloidal metals and semiconductors, with the emphasis falling heavily on the semiconductors. Michael Grätzel contributes an excellent review chapter on interfacial electron transfer reactions in colloidal semiconductor systems that serves very well as an introduction to the field for interested newcomers. Serpone *et al* present a thought-provoking paper on the likely reaction routes involved in valence band hole-driven oxidation processes at colloidal TiO₂ particle surfaces, and Fendler closes the show with an elegant paper detailing the characterization of size quantized CdS and ZnS particulate films.

A criticism of the book is that, apart from one interesting contribution by Mulvaney, Grieser and Meisel, little mention is made of the role of the fundamental property of the zeta potential in colloidal electrochemistry. Mackay makes mention of this in his preface and attempts to justify the absence by referring the reader to other existing texts where the subject has been discussed in more detail. Nevertheless, the lack of such material in a volume of this kind remains a glaring omission and is the book's sole major weakness. However, having said that, the book does cover an extremely wide range of topics and is true to its claim of being the first publication of its kind.

In all, this volume would provide an excellent addition to the bookshelf of any research scientist, development engineer or graduate student working in the areas of colloid science, electrochemistry or related disciplines and the editors are to be congratulated on having assembled so much high quality work between two covers.

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