

## BOOK REVIEW

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### Conducting Polymers A New Era in Electrochemistry

[*Vodljivi polimeri – novo razdoblje u elektrokemiji*]

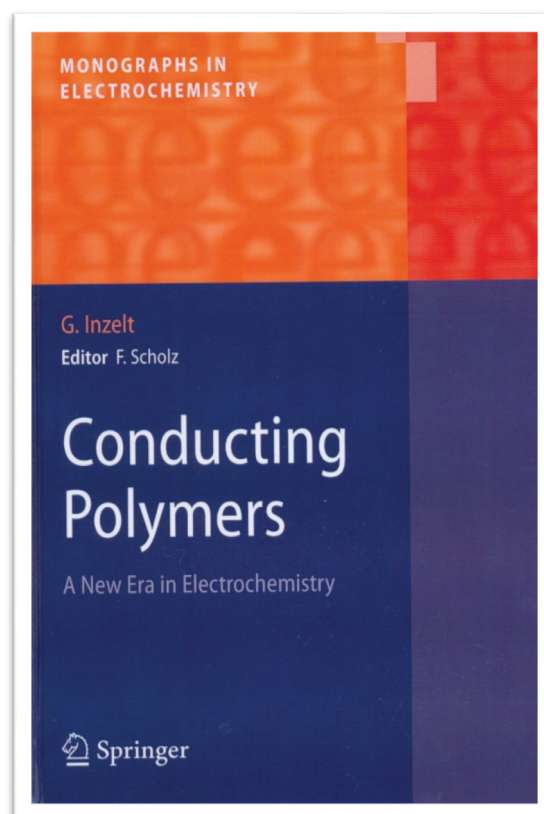
F. Scholz (Ed.), Monographs in Electrochemistry Series,  
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Since the discovery of conducting polymers (CP) there are quite an impressive number of books published on this topic. This is not a surprising fact since conducting polymers belong to a group of materials with very specific and intriguing properties. These materials are especially interesting from the electrochemical point of view, since they are easily prepared, as well as easily manipulated, and characterized by the use of electrochemical methods. Therefore, no wonder that Prof. F. Scholz, the editor of the series, decided to print an additional book on that topic pointing out by the subtitle "A New Era in Electrochemistry" that these materials are interesting for the use in electrochemical devices and practical applications.

The book is organized in 8 Chapters starting with the Introduction as Chapter 1 which, indeed, only introduces us to the history of the field it deals with and supplies 54 references.

Chapter 2, Classification of Electrochemically Active Polymers, starts with the subchapter Redox Polymers as a class of polymers which, due to spatially localized redox sites, can transport electrons by an electron exchange reaction. The subchapter explains the subclasses, their mechanism of electron transport and presents the most investigated representatives of this polymers type.

The second subchapter leads us to Electronically Conducting Polymers (Intrinsically Conducting Polymers – ICPs). In continuation 23 different polymers and their derivatives are presented. Besides, the molecular structure and the mechanisms of their oxidation/reduction paths are given. The major part in the



description is given to the most studied and applied conducting polymers like: polyaniline, polypyrrole, polythiophene *etc.* Further on, Electronically Conducting Polymers with Built-In or Pendant Redox Functionalities, Copolymers and Composite Materials are described. This concludes the chapter describing the materials that are essential to conducting polymers. This Chapter is supported by an impressive number of 776 references.

Chapter 3, Methods of Investigation, is an excellent guide through the numerous methods used in studying conducting polymers. Although it does not deal with each mentioned technique in detail, it points out the most important details necessary to understand the behavior of CP, the mechanism of synthesis, the charac-

ristics of the material obtained, *etc.* The essential electrochemical techniques presented are: cyclic voltammetry, chronoamperometry, chronocoulometry, electrochemical impedance spectroscopy. These techniques often are combined for in situ measurements with other techniques like Electrochemical Quartz Crystal Micro(nano)balance, Radiotracer Techniques, Probe Beam Deflection Technique, Ellipsometry, Spectrometry, Electron Spin Resonance Spectroscopy, Fourier Transformed Infrared Spectroscopy, other spectroscopies, and Surface Plasmon Resonance. For the characterization of the polymerized material, Scanning Probe Techniques are unavoidable, like Scanning Tunneling Microscopy, Atomic Force Microscopy and Scanning Electrochemical Microscopy. To characterize CPs the important parameter is the conductivity of the material, and therefore Conductivity Measurements are included, as well as other techniques. Chapter 3 is supported by 434 references.

In Chapter 4, Chemical and Electrochemical Syntheses of Conducting Polymers are treated. It offers a detailed survey of approaches to synthesis of redox and of intrinsic polymers. To quote the author "...virtually the whole arsenal of synthetic polymer chemistry methods has been exploited". Both chemical and electrochemical syntheses are reviewed. The generation (growth) of polymers is outlined including the influence of media (solvent and supporting electrolyte), and other conditions of influence on the synthesis (*e.g.* potential, different rate of potential cycling in voltammetry, pH of the feed media *etc.*). The importance of the kinetics of the polymer growth and the resulting structure of the layer are stressed out. The work on the syntheses of numerous intrinsic polymers is described. The preparation of copolymers is outlined. 149 references support Chapter 4.

Chapter 5, Thermodynamic Considerations, introduces us to the polymer modified electrodes and to the problems that might arise due to polymer adherence to the substrate surface. A true equilibrium is seldom established, and the thermodynamic treatment should be applied for an idealized situation with some caution. In the succeeding subchapters Neutral Polymer in Contact with an Electrolyte Solution is treated in more detail, followed by Charged Polymer in Contact with an Electrolyte Solution. The second one deals with Nonosmotic Membrane Equilibrium and Osmotic Membrane Equilibrium and Electrochemical and Mechanical Equilibria. Special attention is paid to Mechanical-Electrochemical Equilibrium and Incorporation of Counterions. The equilibrium situation between the surface film and the solution for the ions that enter the film is elaborated in the context of electron exchange reaction taking place. The interaction between the redox sites is elaborated.

The chapter ends with a glance on Dimerization, Disproportionation and Ion Association Equilibria within the Polymer Phase. 28 references are cited in Chapter 5.

Chapter 6, Redox Transformation and Transport Processes, gets into the heart of conducting polymers' nature. The elucidation of these properties may be the most interesting problem of this field (G. I.). The complexity of these systems is taken into consideration through a number of possible aspects. The model of charge transfer and charge transport processes through the polymer is elaborated and these phenomena are treated in the following subchapters:

Electron Transport for the Electron Exchange Reaction, and separately the Electronic Conductivity, is described. The difference between redox polymers and electronic conductive polymers is explained. The latter ones, consisting of typically polyconjugated, polyaromatic or polyheterocyclic molecules, show a drastic change in conductivity (up to 10–12 orders in magnitude) upon oxidation (less frequently reduction). The accompanying features are presented through the work done by a number of authors.

Ion Transport subchapter explains the role of ions, since the overall polymer phase retains neutrality during redox reactions. Some reaction schemes are given for the reduction and for the oxidation processes, as well as examples of the voltammetric behavior in parallel with EQCM measurements of selected CPs. The research on CPs, done by a number of scientists, using various available techniques, is presented in quite a detail.

Coupling of Electron and Charge Transport describes coupled processes in order to keep electroneutrality. The possible mechanisms of electron transfer are taken into account.

Among Other Transport Processes the attention is paid to Solvent Transport, and to Dynamics of Polymeric Motion.

Subchapter 6.5 entitled Effect of Film Structure and Morphology deals with the situation in the swollen polymer films, where microscopic techniques have revealed heterogeneity of the surface layer, consisting of macro- and nano-pores. The situation regarding the space-charge region, transport properties, the role of coulombic attraction, *etc.*, is reviewed. Possibilities of using different models for description of the film (homogeneous, porous) are noted. The possible complex events taking place in such a system are described.

The importance of Thickness is shortly mentioned, while Synthesis Conditions and Nature of the Electrolyte is more thoroughly elaborated. The influence of different factors (solution, solvent, counter-ions, anions *etc.*) on film morphology is well documented.

Subchapter 6.6 deals with Relaxation and Hysteresis Phenomena which is well supported by a number of researches done. And the last subchapter Measurements of the Rate of Charge Transport refers to the studies of electrochemically active polymer by transient techniques. Chapter 6 is supported by 240 references.

Chapter 7, entitled Applications of Conducting Polymers presents the retrospective of all the research done in application of these special materials. The first subchapter, Material Properties of Conducting Polymers, deals with all the interesting properties of CP, and the circumstances under which they can be changed or handled. It goes for conductive/nonconductive state, change of colors depending on oxidation state, conductivity, *etc.* The next subchapter deals with Application of Conducting Polymers in Various Fields of Technologies. It includes Thin-Film Deposition and Microstructuring of Conductive Materials (Antistatic Coating, Microwave Absorption, Microelectronics) supplied with the corresponding examples. Further on, Electroluminescent and Electrochromic Devices is elaborated, where a detailed guide through the application possibilities in that area is reported. Due to its structure and charge conductive polymers are suitable for Membranes and Ion exchanger devices, and due to its characteristic potential of the stable oxidized form, they offer a good Corrosion Protection. A special attention is paid to the particularly suitable area for CPs and that is Sensors. Due to the sensitivity towards different oxido/reductive surroundings, potential differences, *etc.*, CPs are used as Gas Sensors, in Electroanalysis and Biosensors. They are Materials for Energy Technologies, *i.e.* they are used in batteries as active electrodes, and also as photovoltaic devices.

A survey is given on the researches that have been carried out on the application of Cs as Artificial Muscles, due to their quality of reversible swelling is. The chapter ends with the Electrocatalysis, the area which offers "endless ways to design tailor-made electrodes for specific catalytic purposes which make this approach highly attractive" (G. I.). Quite a number of examples in electrocatalysis are presented. Chapter 7 ends with the list of 373 references.

Chapter 8, Historical Background (Or: There Is Nothing New Under the Sun) reminds us that even before the great trio (Shirakawa, McDiarmid and Heeger), who earned Nobel Prize for the discovery of conductive polymers, certain conductive polymers were produced, studied and even applied. So, is there really anything new under the Sun? No, there is not, but we have not been aware of CPs, as of the materials that offer a variety of new possibilities. So the real era of conductive polymers chemistry/electrochemistry has started actually thanks to a student mistake, and clever scientists who learn on/from mistakes.

The book presents a valuable guide through the great deal of the research done on conductive polymers, and although it might not be the easiest book for student to study from, it is definitely welcome to the researchers as a precious stock of 1633 references!

Short biographies of Profs György Inzelt and Fritz Scholz are included in the book. The book is supplied by Name Index, and also a Subject Index, which makes it easy to use the book.

*Ljerka Duić*