

Electroactive Polymer Electrochemistry

Part 1 Fundamentals

**Edited by
Michael E. G. Lyons**

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Electroactive Polymer Electrochemistry

Part 1: Fundamentals

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Preface

The development of “tailormade” electrode surfaces using electroactive polymer films has been one of the most active and exciting areas of electrochemistry over the last fifteen years. The properties of these materials have been examined by a wide range of scientists from a variety of perspectives, and now electroactive polymer research is considered to be a reasonably mature area of research endeavor. Much is now understood about the fundamental mechanism of conduction in these materials. A wide range of electrochemical techniques may be used to probe the conductivity processes in these materials, and more recently, a number of *in situ* spectroscopic techniques have been used to further elucidate the structure of these materials. The *in situ* spectroscopies and allied techniques have also been used to obtain correlations between structure and redox activity. The applications found for electroactive polymers are many and varied, and range from thin film amperometric chemical and biological sensors, electrocatalytic systems, drug delivery devices and advanced battery systems through to molecular electronic devices.

The research literature on electroactive polymers is truly enormous and can daunt even the most hardened researcher. The vast quantity of material reported in the literature can also intimidate beginning graduate students. Hence the present book. The original idea for this book arose as a result of a series of lectures on chemically modified electrodes and electroactive polymers given by the writer to final year undergraduates at

Trinity College Dublin. At the time (1991) the only course material available was the original literature and a few review articles. When faced with such a situation one has to bite the bullet and do something about it. Hence the present endeavor was conceived. It is hoped that the present volumes will prove useful for advanced undergraduate/first year graduate courses in electrochemistry/materials science. The material was written with the demands of graduate students very much in mind, and the individual chapters are written at a level that graduate students will appreciate.

Active research scientists are very busy people and the editor has been fortunate to have been able to persuade a number of the leading contributors to the development and understanding of electroactive polymer materials to contribute to this project. I thank them for their labors and for the first-rate contributions produced.

A single volume work was originally envisaged. However, as the project proceeded it was realized that the area of electroactive polymer electrochemistry was too wide ranging to be encompassed within the covers of a single volume. It was therefore decided to produce a three-part work. The first part (Chapters 1 to 4) presents a survey of the fundamental principles underlying the electrochemical behavior of electroactive polymer materials. In this volume the fundamentals of charge percolation and conductivity behavior allied with the membrane properties of electroactive polymer films is presented in some detail. Furthermore the phenomenon of heterogeneous redox catalysis at electroactive polymer modified electrodes is discussed. In Part 2 (Chapters 5 to 11) the topics of methodology and applications of electroactive polymer films is addressed. Finally in Part 3, the important topic of polymer ionics is discussed. This topic is currently of much interest and has led to the invigoration of the classical subject of ionics. At the time of writing, Part 3 is still in the planning stage.

Part 1 dealing with fundamentals begins with a long chapter by Lyons, outlining both the fundamental mechanisms of charge percolation in electroactive polymer films, and the various techniques which may be used to quantify the kinetics of charge percolation. The various theoretical models used to describe redox conduction are presented in detail. Furthermore the quantitative aspects of the various techniques used to examine charge percolation are also addressed. In Chapter 2 (Lyons) a number of theoretical models describing electrocatalysis using electroactive polymer films is presented. The approach here is to show in some detail how one can set up simple models which capture the essence of the electrocatalytic process and subsequently solve the diffusion/reaction equations to produce approximate analytic expressions for the current

response in terms of system specific parameters. In Chapter 3 (Doblhofer and Vorotyntsev) the membrane properties of electroactive polymer films are discussed in careful detail. This is a very important topic and the authors have been leading exponents of the methods discussed in the contribution. The conduction behavior of redox polymers is well understood in terms of intersite electron hopping. In contrast, the situation for electronically conducting organic polymer materials is not as well resolved. In the final chapter of Part 1, Albery and Mount (Chapter 4) present a lucid discussion of their dual rail transmission line approach which can be used to model the mixed conduction (electronic/ionic) behavior of electroactive polymers. Much of the material presented in this chapter has been only recently developed by the authors and the material contains many novel insights and ideas.

The emphasis changes in *Electroactive Polymer Electrochemistry, Part 2: Applications* where methodology and applications is addressed. The volume begins (Chapter 5) with a contribution by Morton-Blake and Corish. These contributors have been very active in the area of atomistic simulation of matter transport phenomena in solid materials. In the present contribution they describe in a lucid manner the results of their recent work in applying the methodology of atomistic simulation to quantify dopant transport processes in electroactive polymers. The idea of simulation is continued in Chapter 6, where Cassidy carefully describes the application of digital simulation protocols to charge transport in electroactive polymer films. A novel feature of this chapter is the inclusion of detailed FORTRAN computer codes for a number of specific problems often encountered in practice.

The contribution by Higgins, Christensen and Hamnett (Chapter 7) is very timely and discusses *in situ* ellipsometry and FTIR spectroscopy applied to electroactive polymer modified electrodes. These co-authors have been particularly active in the latter area, and their overview, although brief, conveys many original insights.

In Chapter 8, co-authored by Kelly and Vos, the electrochemical behavior of osmium and ruthenium poly(pyridyl) redox polymers is discussed in some detail. Vos has made significant contributions in this area. This chapter ties in well with the more general discussion presented by Lyons in Chapters 1 and 2, in that many of the theoretical concepts addressed in the latter chapters are again discussed by Kelly and Vos with specific reference to redox active metallopolymer materials.

In Chapter 9, Bartlett and Cooper discuss the applications of electroactive polymers in bioelectrochemistry and bioelectronics. This is a very exciting and rapidly developing field, and it is proper that the volume includes this topic. Electroactive polymer materials will feature

strongly in future developments in this area. Again Bartlett and Cooper have made major contributions in this field.

In Chapter 10, Leech discusses the analytical applications of polymer modified electrodes. In Chapter 11, the analytical theme is continued and again, Smyth and Iwuoha survey the applications of electroactive polymers in electroanalytical chemistry. In this case the important area of biosensors is examined. The areas described in these chapters have attracted significant research activity in recent years, and the material presented in these chapters is timely, and is written by well known and experienced practitioners in the field.

The editor is grateful to the senior editor of Plenum Press, Ms. Amelia McNamara, for her patience in waiting for the book when deadlines were long, long overdue. Our production editor, Mr. Tony Orrantia is also to be thanked for his patience and skill. The many workers at Plenum have worked hard on this project to produce an excellent result. One begins a project such as this with high hopes and over optimistic expectations with respect to the length of time required to complete the project. One quickly learns that the task of an editor is onerous and time consuming, and that events conspire to thwart smooth progress with increasing frequency as the deadline approaches. Perhaps there is a new physical law to be discovered here!

I finally would like to acknowledge the help and support of my wife, Catherine and my children, Michelle and Edward. Many precious hours were stolen from them during this project. Daddy has now stopped working at the computer screen, for the time being at least. I now hope to resume those long walks along Bray Head with all the family, now that this work has finally come to fruition.

Michael Lyons

Dublin

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Charge Percolation in Electroactive Polymers

Michael E. G. Lyons

1. INTRODUCTION

Electroactive polymer films have attracted considerable attention in the electrochemical community in recent years due largely to the wide range of possible applications of these materials in electrocatalysis, molecular electronics, chemical and biosensor technologies, energy conversion and storage, and as media for controlled drug release.

A number of useful reviews have previously been published. The review by Murray⁽¹⁾ provides a good summary of early work in the area, and reviews by Alberly and Hillman⁽²⁾ and Hillman⁽³⁾ are also useful. More recent reviews have been written by Abruna,⁽⁴⁾ Evans,⁽⁵⁾ Smyrl and Lien,⁽⁶⁾ Kaner,⁽⁷⁾ Pethrick,⁽⁸⁾ and on a more general level by Lyons.⁽⁹⁾ A monograph on the electrochemistry of electroactive polymers has recently been published under the editorship of Murray.⁽¹⁰⁾ This volume contains a useful chapter by Majda⁽¹¹⁾ on the dynamics of electron transport in polymeric assemblies of redox centres. In the same volume a chapter coauthored by Oyama and Ohsaka⁽¹²⁾ surveys experimental methods used to quantitate transport in electroactive polymer films. There is much useful experimental data tabulated in this work. In the same volume Murray⁽¹³⁾ gives a comprehensive overview of the electrochemistry of electroactive polymers, whereas the contribution by

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Andrieux and Saveant⁽¹⁴⁾ considers electrocatalytic applications, which are the subject of Chapter 2 of this book. A recent volume of Faraday Discussions⁽¹⁵⁾ dealing with charge transfer in polymeric systems is also of interest; it contains a good overview of progress in the area up to 1989.

Electroactive polymers can be classified into three major types: redox polymers, electronically conducting polymers (plastic metals), and loaded ionomers. For the purposes of this discussion, we consider thin films of electroactive polymers deposited onto the surface of a support electrode. The combination of deposited polymer film and support constitutes a chemically modified electrode. The latter involves the deliberate immobilization of a chemical microstructure on a host electrode surface to perform a specific task. Hence we are dealing with tailor-made electrochemistry using surface-deposited multilayer redox active microstructures. In particular we discuss the mechanism of charge percolation through surface-deposited polymer films. This topic is of central importance, since the rate of charge percolation through the polymer matrix generally dictates operational characteristics of the deposited microstructure when used in a practical application. In this chapter we discuss the fundamentals of charge percolation in thin electroactive polymer layers and describe a number of electrochemical techniques that can be used to quantify the rate of charge percolation in these materials. The allied topic of heterogeneous mediated electrocatalysis using surface deposited electroactive polymer films is discussed in some detail in Chapter 2.

We do not discuss however the important field of polymer ionics and polymer electrolytes. This class of materials consists of polar macromolecular solids in which one or more of a wide range of salts has been dissolved. A classic example that has been studied a great deal is the combination of poly(ethylene oxide) (PEO) containing LiX salt as solute. The reader is referred to a recent monograph edited by Scrosati^{(16(a))} and to review articles by Vincent,^{(16(b))} Linford,^{(16(c))} Owen^{(16(d))}, and to a volume edited by MacCallum and Vincent^{(16(e))} for further information on this rapidly expanding area of polymer science. The major focus in this chapter (and indeed in this book) is on electroactive polymers used as *electrode materials*. Polymeric electrolytes, although important in both a technological and fundamental sense, present different problems to those discussed in this volume, and so we restrict discussion to electroactive polymer-based chemically modified electrodes.

Early work on chemically modified electrodes concentrated on monolayer derivitized surfaces. In this case reaction was confined to a two-dimensional region near the electrode surface. From a catalytic

viewpoint, this is not a very effective strategy, since homogeneous chemical reactions occur in a three-dimensional zone. Consequently the reaction flux is much greater. However if we use a multilayered polymer film, we obtain a three-dimensional dispersion of redox active-sites throughout the redox active material. Consequently a high local concentration of redox active sites is achieved, even though the total amount of active material is small, ca. $10^{-7} \text{ mol cm}^{-2}$. For a layer typically $1\text{-}\mu\text{m}$ thick, the redox site concentration can be quite high. The following calculation is instructive. The site concentration c (units: mol cm^{-3}) is given by $c = \Gamma/L$, where Γ is the surface coverage (units: mol cm^{-2}) and L is the layer thickness. Hence for $\Gamma = 10^{-7} \text{ mol cm}^{-2}$ and $L = 10^{-4} \text{ cm}$, $c = 10^{-3} \text{ mol cm}^{-3} = 1.0 \text{ M}$. In contrast the surface coverage for a monolayer derivitized system is a factor of 1000 less, with $\Gamma = 10^{-10} \text{ mol cm}^{-2}$. Hillman⁽³⁾ notes that passing a current of 1 A cm^{-2} from a typical film containing $10^{-7} \text{ mol cm}^{-2}$ of redox sites acting as a catalytic mediator requires a turnover rate of 100 s^{-1} . This number implies many turnovers for a useful layer lifetime.

A number of examples of typical electroactive polymer materials are illustrated in Fig. 1.1. Let us examine some general characteristics of each type of material. Redox polymers are localized state conductors, containing redox-active groups covalently bound to an electrochemically inactive polymeric backbone. In these materials electron transfer occurs via a process of sequential electron self-exchange between neighboring redox groups. This process is termed electron hopping. In contrast with electronically conducting polymers, the polymer backbone is extensively conjugated, which results in considerable charge delocalization. Charge transport (via polarons and bipolarons) along the polymer chain is rapid, and interchain charge transfer is rate-limiting. Redox polymers, such as poly(vinyl ferrocene), exhibit the interesting effect of remaining conductive over only a limited range of potential. Maximum conductivity is observed when concentrations of oxidized and reduced sites in the polymer are equal. This occurs at the standard potential of the redox centres in the polymer. It is a characteristic of redox conduction. In contrast electronically conducting polymers, such as poly(pyrrole), display quasi-metallic conductivity and remain conductive over an extended potential range. The window of conductivity is governed to a large extent by the chemical nature of the polymer, and it can therefore be synthetically controlled. Redox polymers are usually preformed and subsequently deposited onto the support electrode surface via dip or spin coating. In contrast electronically conducting polymers are usually generated via *in situ* electrodeposition. In this case there is electropolymerization of a redox-active monomer. However we can also form redox