MOLECULAR DESIGN OF ELECTRODE SURFACES

EDITED BY
ROYCE W. MURRAY

TECHNIQUES
OF CHEMISTRY
VOLUME XXII

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A WILEY-INTERSCIENCE PUBLICATION
JOHN WILEY & SONS, INC.
New York • Chichester • Brisbane • Toronto • Singapore

Library of Congress Cataloging in Publication Data:

Murray, Royce W.
Molecular design of electrode surfaces / Royce Murray.
p. cm.—(Techniques of chemistry; v. 22)
"A Wiley-Interscience publication."
Includes bibliographical references and index.
ISBN 0-471-55773-0
1. Electrodes—Design and construction. 2. Surface chemistry.
I. Title. II. Series.
QD61.T4 vol. 22 1992
[QD571]
542 s—dc20
[541.3'724] 91-25499
CIP

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1
Printed and bound by Malloy Lithographing, Inc.

TECHNIQUES OF CHEMISTRY

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VOLUME XXII

MOLECULAR DESIGN OF ELECTRODE SURFACES

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INTRODUCTION TO THE SERIES

Techniques of Chemistry is the successor to Technique of Organic Chemistry and its companion, Technique of Inorganic Chemistry. The newer series reflects the fact that many modern techniques are applicable over a wide area of chemical science. All of these series were originated by Arnold Weissberger and edited by him for many years.

Following in Dr. Weissberger's footsteps is no easy task, but every effort will be made to uphold the high standards he set. The aim remains the same: the comprehensive presentation of important techniques. At the same time, authors will be encouraged to illustrate what can be done with a technique rather than cataloging all known applications. It is hoped in this way to keep individual volumes to a reasonable size. Readers can help with advice and comments. Suggestions of topics for new volumes will be particularly welcome.

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PREFACE

The notion of synthetically attaching electron transfer and catalytically active molecules to electrode surfaces is now well into its second decade of research and exploration. Interest in chemically modified electrodes shows no signs of abating and indeed novel off-shoots of the original ideas continue to appear each year. There is hardly a facet of electrochemical science that has been untouched by the now-accepted ability to design and control the molecular character of electrode interfaces. The literature of the subject has become sufficiently massive that single review articles in practical terms have great difficulty in explaining all of the important ideas of electrode modification. It thus seems timely to incorporate these ideas into a larger and more detailed volume, which we offer here to interested readers.

I was fortunately able to persuade many of the leading contributors to the development and understanding of molecularly designed electrodes to contribute to this volume. I gave them substantial freedom in their choice of topic. This produced inevitably some overlap between chapters, and a few gaps, but also it produced chapters that reflect the special flavor of insight that writing by leading research scholars entails. I was additionally delighted to find many original insights embedded in the chapters, and insights that clarify current literature issues; I hope that readers both novice and expert will enjoy discovering them.

I prepared Chapter I to set the stage with some of the motivations for molecular electrode design (i.e., why does this subject exist?), an introduction to some concepts of electroreactivity of molecules attached to electrode surfaces, and a general review of chemical tactics for surface attachments and the types of thus attached molecules. Next follows a chapter by Salaita and Hubbard (Chapter II) on using adsorption to immobilize organic species on well-defined electrode surfaces. Professor Hubbard carried out seminal experiments on using chemisorption to modify electrode surfaces. This chapter presents a summary and progress report of his subsequent experiments quantifying and analytically characterizing adsorption in the light of the atomic order of the metal electrode surface and the chemical reactivities that adsorption reflects. Chapter III, prepared by Facci, explains a different type of monomolecular adsorption, which is controlled substantially by hydrophobic interactions. This subject includes so-called self-assembled films and those prepared by spreading and compression of monolayers in Langmuir troughs. This area is a recently blossomed one with a particularly active research profile.

Chapter IV, by Majda, begins descriptions of electrodes coated with multimolecular layers of electron-transfer active sites, so-called redox polymers. These molecular films entail fascinating issues of how electrons hop from donor to acceptor sites and what forces and chemical effects govern the rate at which such electron self-exchange reactions occur. This chapter is followed by Chapter V by Andrieux and Savéant, which presents theoretical aspects and experimental examples of redox and chemical catalysis at redox polymer coated electrodes. The electrocatalytic oxidation–reduction of a substrate species by an electroactive molecular film potentially depends on quite a variety of different kinetic events: electron hopping, permeation, boundary crossing, as well as the catalytic reaction itself. Understanding how these interplay is important in considering applications of modified electrodes to catalysis. Chapter VI, by Bard and Mallouk, describes a relatively recent development in electrode surface design, the use of clays and zeolites as modifying layers. These layers add to the chemical reactivity features of designing electrodes, the element of steric selectivity with which reactants can penetrate the ordered lattices of clays and zeolites.

Chapter VII, by Leidner, describes a particular type of electron-transfer mediation reaction using redox polymer films, designed to reveal their free-energy rate connections. Oyama and Ohsaka, in Chapter VIII, expand on Majda's introduction to charge transport in redox polymers, in describing additional methodology to charge-transport studies and a useful survey of many of the results that have been obtained. The closing chapter, Chapter IX, by Martin and Van Dyke describes another element of molecular design of electrodes, as embodied in electronically conducting polymers. Martin particularly focuses on important aspects of proper measurement of the kinetics of charge transport in these important materials.

I am exceedingly grateful to these scholars for preparation of these chapters on the molecular design of electrode surfaces. I am also grateful to Mrs. Kathy Justice for her help in keeping this project and my office organized, and to my student Hong-hua Zhang for her expert assistance with artwork.

ROYCE W. MURRAY

Chapel Hill, North Carolina
January 1992

CONTENTS

Chapter **I**

INTRODUCTION TO THE CHEMISTRY OF MOLECULARLY DESIGNED ELECTRODE SURFACES

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1.1 SOME MOTIVES FOR MOLECULARLY DESIGNED ELECTRODE SURFACES

The beauty of electrochemical oxidation and reduction reactions is that one can employ the electrode potential as a source or sink of pure, uncomplicated electrons of flexibly chosen free energy. In a thermodynamic sense, such control permits predictive inciting of oxidation–reduction reactions according to their

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Molecular Design of Electrode Surfaces,
Edited by Royce W. Murray. Techniques of Chemistry Series, Vol. XXII.
ISBN 0-471-55773-0

free-energy characteristics. This beauty is indeed realized for so-called reversible, outer-sphere, one-electron-transfer reactions. For example, changing the potential of a Pt electrode in an equimolar, aprotic solution of *p*-benzoquinone and its radical anion to a value slightly more negative than the equilibrium potential, causes a reduction current to flow. First the electrode–solution interphase, and eventually the entire cell solution, become enriched in the reduced form $Q^{\cdot -}$ to an extent predictable by the applied potential and the Nernst equation. Resetting the electrode potential to the original, equilibrium value, results in an oxidation current that restores the electrode–solution interphase and eventually the entire cell solution to the original equimolar $Q/Q^{\cdot -}$ composition. The ability to recover the original composition defines this reaction as *chemically reversible.* If the rate of the electron-transfer reaction is faster than any other step in the process (such as diffusion to the electrode), the electrode reaction is also referred to as an *electrochemically reversible* reaction, at least in the practical sense (1).

Then again, the beauty of reversible electrochemistry often gives way to the reality of finite chemical and electrochemical reaction kinetics. Many electrochemical oxidation–reduction half-reactions exhibit slow heterogeneous reaction kinetics and are termed *electrochemically irreversible* (i.e., *not* reversible). Furthermore, the kinetics of a particular electrochemical reaction, and sometimes even the eventual electrode reaction product, can also depend on the composition of the electrode. In that case, the electrode serves as a chemical reagent. For example, the electrochemical reduction of hydrogen ion occurs rapidly and reversibly at a (clean) Pt electrode surface, but its reaction kinetics are very slow at a Hg surface. There is a chemical reason for the difference; an H-atom bound surface intermediate is formed with favorable energetics and kinetics on Pt but not on Hg. On Hg, the electron free energy must be greatly elevated (i.e., more negative potentials applied) to produce a rapid H^+/H_2 reaction; the extra potential is called an *over-potential.* The H^+/H_2 reaction illustrates the role of the electrode surface in electrochemical catalysis, or *electrocatalysis.*

Seeking understanding and control of electrochemical reaction kinetics and catalysis has motivated electrochemical research for decades. Much research in the 1950s and 1960s was directed at choosing different metal alloy electrode surfaces to somehow increase the rates of desired reactions. Many fundamental aspects of electrode reaction kinetics were elucidated during these studies (2, 3). The relation of metal H-atom binding to H_2 reaction kinetics (4) was only one example of how surface binding (*adsorption*) exerts a strong influence on the electrode kinetics of numerous organic and inorganic electrode reactions. A constraint on classical approaches to electrocatalysis of slow reactions was the requirement for an electronically conducting electrode, that is, a metal or carbon. This constraint severely limited the repertoire of surface chemistry available for electrocatalytic purposes.

A new approach to electrocatalysis emerged in the mid-1970s from studies in which electrochemically reactive molecular materials were attached to electrode surfaces (5–13) using systematic synthetic chemistry. Access to molecular electrode surfaces generated, in effect, an enormous diversification in the nature of electrode surfaces. Choice of the applied potential determines whether the attached molecules are in the electron donor or acceptor forms. The electrode reactions of the target *substrate* species now occur on a *molecular* electrode surface, whose reactivity towards the substrate is now a hopefully more *predictable* subject. This is a crucial point; by choice and design of the attached molecules, we have new ways by which to seek appropriate forms of substrate binding, intermediate states, steric effects, and so on, that lead to a rapid electrode reaction of the substrate. With such electrodes, which were dubbed *chemically modified electrodes* (14–16), the problem was transformed from one of surface metal atom chemistry into a problem that could be addressed using rational choices of chemical reactivities of known non-immobilized catalyst molecules that are capable of binding substrates and of delivering electrons. By and large, reactivities of non-immobilized electron-transfer molecules are preserved when immobilized on an electrode. The chemical diversity of electrochemical science was greatly enlarged by this transformation of the problem.

Electrocatalysis of the reduction of molecular dioxygen (O_2) is an important illustration of the benefits of choice and design of molecules attached to electrode surfaces. The synthetic efforts of Collman, Anson, and their co-workers (17–22) produced a dimeric cobalt porphyrin, termed Co_2FTF4 (Fig. 1.1, lower structure) designed, in its reduced state, to be a multiple electron donor and to exhibit an affinity for binding of O_2. When this molecule was immobilized (by chemisorption) on a carbon electrode surface, the resulting modified electrode was shown to effect a four-electron reduction of O_2 to water. Rotated ring–disk voltammetry in Fig. 1.1*b* illustrates this process. The potential of the electrocatalytic O_2 reduction wave reflects that required to produce the oxygen-binding catalytically active porphyrin state (22). The research indicated (20) that the Co(III)Co(II)(Por) (Por = porphyrin) form of the molecule strongly binds O_2. It is possible then that formation of this adsorbed species is the leading step in a subsequent series of proton and electron-transfer reactions that culminate in the formation of water. A crucial point was minimal escape of intermediate states of reduction (viz., H_2O_2) from the porphyrin cavity (wherein the reaction ostensibly occurred). In the absence of the porphyrin layer, with monomeric porphyrins, or, with those of nonoptimum binding characteristics (Fig. 1.1*a*), O_2 reduction on the carbon electrode is both slower and at comparable potentials yields H_2O_2 as the primary (two-electron) reaction product. Other examples of analogously designed four-electron chemistry have since appeared (22, 23).

Electrocatalysis has been a continuing, strong theme of chemically modified electrode research. Its principles and experimental progress are discussed by Andrieux and Savéant in Chapter V. Modified electrode research has taken much more diverse, and still-widening directions, however, both practical and fundamental (5–13). Electrode modification involves chemical synthesis and reactivity studies (24, 25) on thin molecular films, including monomolecular layer films; this topic has been a frontier in other areas as well, such as

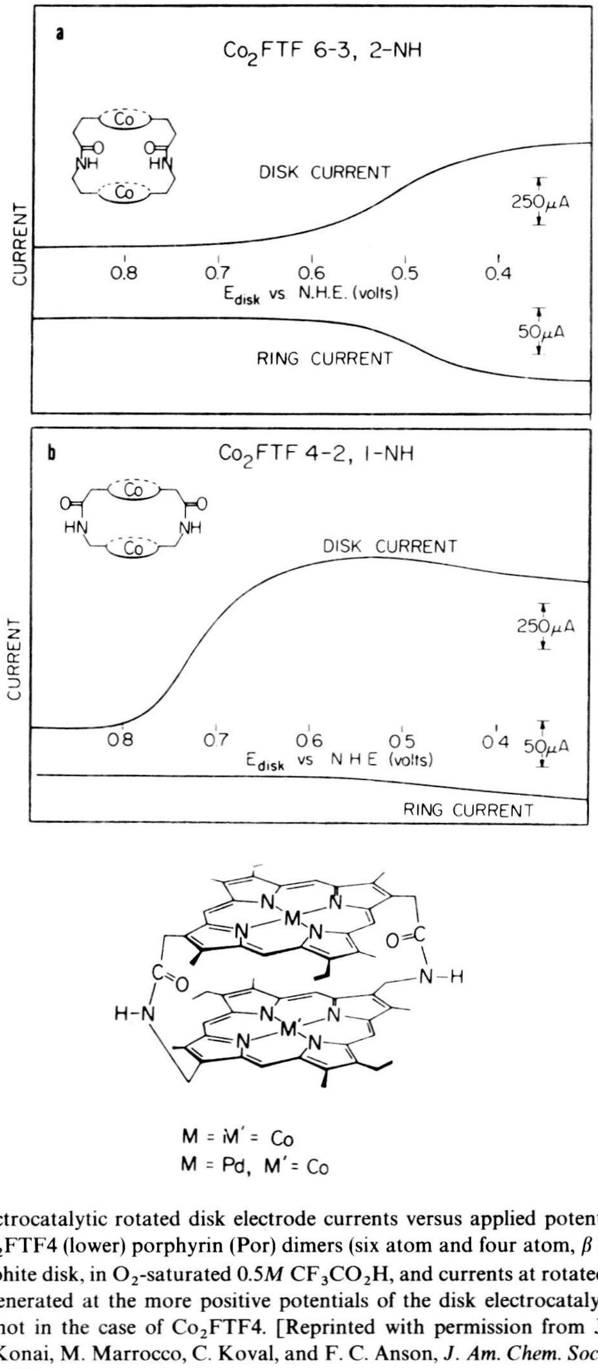

Figure 1.1. Electrocatalytic rotated disk electrode currents versus applied potential for Co_2FTF6 (upper) and Co_2FTF4 (lower) porphyrin (Por) dimers (six atom and four atom, β linked) coated on the rotated graphite disk, in O_2-saturated 0.5*M* CF_3CO_2H, and currents at rotated Pt ring showing that H_2O_2 is generated at the more positive potentials of the disk electrocatalysis in the case of Co_2FTF6 but not in the case of Co_2FTF4. [Reprinted with permission from J. P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval, and F. C. Anson, *J. Am. Chem. Soc.*, **1980**, *102*, 6027. Copyright © (1980) American Chemical Society.]

biomembranes and the surfaces of polymeric materials. Modified electrode surfaces have been both models and targets for modern and novel approaches to surface analysis and structure (26–40). The introduction (41–46) of electroactive polymer films on electrodes provoked considerable research on synthetic and electropolymerization assembly of polymeric metal complexes (12, 13) and on mass and electron transport inside mixed-valent polymer films (47). It is possible to fruitfully design electrode surfaces with, on the one hand, electroanalysis (48–50) in mind and on the other aiming at photocorrosive protection of semiconductor electrodes (51–53). Controlling the physical spacing between the electrode atoms and an attached electron donor or acceptor (54–58) is an important entré into the basics of long-range electron transfer and of the relation of the "double layer" to electrode reactions. Other forms of spatial control of electrode-attached chemicals lead to rectifying molecular junctions, molecular transistors, and other features of molecular electronics interest (59–60). There has been great interest in electrochemical formation of films of so-called conducting polymers and of their electrochemical properties (61–65).

The following chapters expand upon many aspects of modified electrodes. The purpose of the remainder of this introductory chapter (Chapter I) is to give the reader an outline of the chemistry of electrode surface modifications and their relevance to the various areas of study of modified surfaces. Suffice it to say that the topic of molecular design of electrode surfaces has expanded tremendously beyond its beginnings and is a now strongly established component of electrochemical science.

1.2 ATTACHING AND USING MOLECULES ON ELECTRODE SURFACES

1.2.1 What "Immobilization" Means

Molecular surface design necessarily involves some form of molecular immobilization on the electrode surface. In the modified electrode context, immobilization actually refers to several interwoven goals, not all of which may be successfully attained, or even desired. First, one generally seeks a *physically and chemically stable immobilization* of the target molecule. Characterization of this stability is an important component of researching the surface preparation. Typical criteria are that the "immobilized" species remain on the electrode surface when contacted or washed by an electrolyte solution, and when the potential of the electrode is varied between values leading to useful electroactivity. Important characteristics of immobilized electroactive molecules are their stability upon repeated oxidation and reduction, and good chemical and electrochemical reversibility. An equivalent criterion refers to use in an electrocatalytic reaction; the surface molecule should stably survive many reaction turnovers in the catalytic scheme. Some applications may, on the other hand, actually aim to electrochemically provoke a controlled *detachment* of the immobilized molecules, as in using the electrode surface as a microscopic reagent source (66).

Second, the term "immobilization" is usually employed in a macroscopic sense and does not (necessarily) denote absence of molecular-scale mobility of the surface molecule. For example, there are many cases (5–7) of monolayers of electroactive electron donors or acceptors attached to the electrode surface by insulating but flexible molecular chains. While such donor–acceptor sites may have a noncontacting equilibrium spacing from the underlying electrode, they apparently still possess thermal fluctuations for sufficiently close approach to yield facile electron transfers with the electrode (5–7, 67). These molecules are accordingly immobilized at, but not with respect to, the electrode. In other, and more recent, monolayer cases (54–58), in which the molecular connectors are both insulating *and* nonflexible, the electron donor–acceptor couple may be sufficiently immobilized with respect to the underlying metal electrode surface, that electron transfers are constrained to larger than contact distances. When electrodes are coated with electroactive polymer films, multiple monolayers of the target immobilized molecules are present, some adjacent to but most others remote from the electrode. When the target molecules are counterions of an ion-exchange polymer film, they are immobilized by the film, but may nonetheless diffuse within it (46, 68, 69) to the electrode surface. Thus, "immobilization" is more an operational than a molecularly descriptive term, and there can be many interesting microscopic elements of transport remaining for the researcher of a newly immobilized molecular design to uncover.

Electrode-immobilized molecular species fall into three broad categories: *monomolecular layers*, *multimolecular layers*, and *spatially defined, molecularly heterogeneous layers*. A further categorization can be made with respect to the electronic character of the electron donor–acceptor sites. Polymeric, multilayer species with *delocalized electronic states*, such as poly(pyrrole) (63–65), are usually referred to as *conducting polymers* (61, 62). Molecular layers in which the donor–acceptor sites are electronically well defined and localized as molecular states, such as ferrocene or the dicobalt porphyrin in Fig. 1 are referred to as *redox monolayers* or *redox polymers* (5–13). Most of the material in this volume will refer to electronically localized, immobilized redox species, although conducting polymers are also often used in molecular electrode design.

The manner of preparation and the uses of monomolecular layers, multimolecular layers, and spatially defined, molecularly heterogeneous layers are generally distinctive to each category, as will be indicated in the sections that follow. In our discussion of immobilization chemistry and applications, the intent is to liberally provide appropriate illustrations, but not comprehensively catalog the extensive literature on the subject. We apologize in advance to authors whose work is not included.

1.2.2 Cyclic Voltammetry of Immobilized Redox Molecules

Before proceeding further, it will be useful to outline the cyclic voltammetric behavior of immobilized, electroactive molecules on electrodes. Cyclic voltammetry is the method most commonly employed to characterize the electron-transfer activity of electroactive films.

Figure 1.2 is a commonly used schematic of electron transfers in surface films of electronically discrete redox molecules (e.g., an immobilized ferrocene species). Figure 1.2*B* refers to monolayer films; Fig. 1.2*C* and *D* represent multimolecular layers, and Fig. 1.2*A* shows a cyclic voltammogram of a reversibly reacting redox (Ox and Red) layer (monolayer or multilayer) with

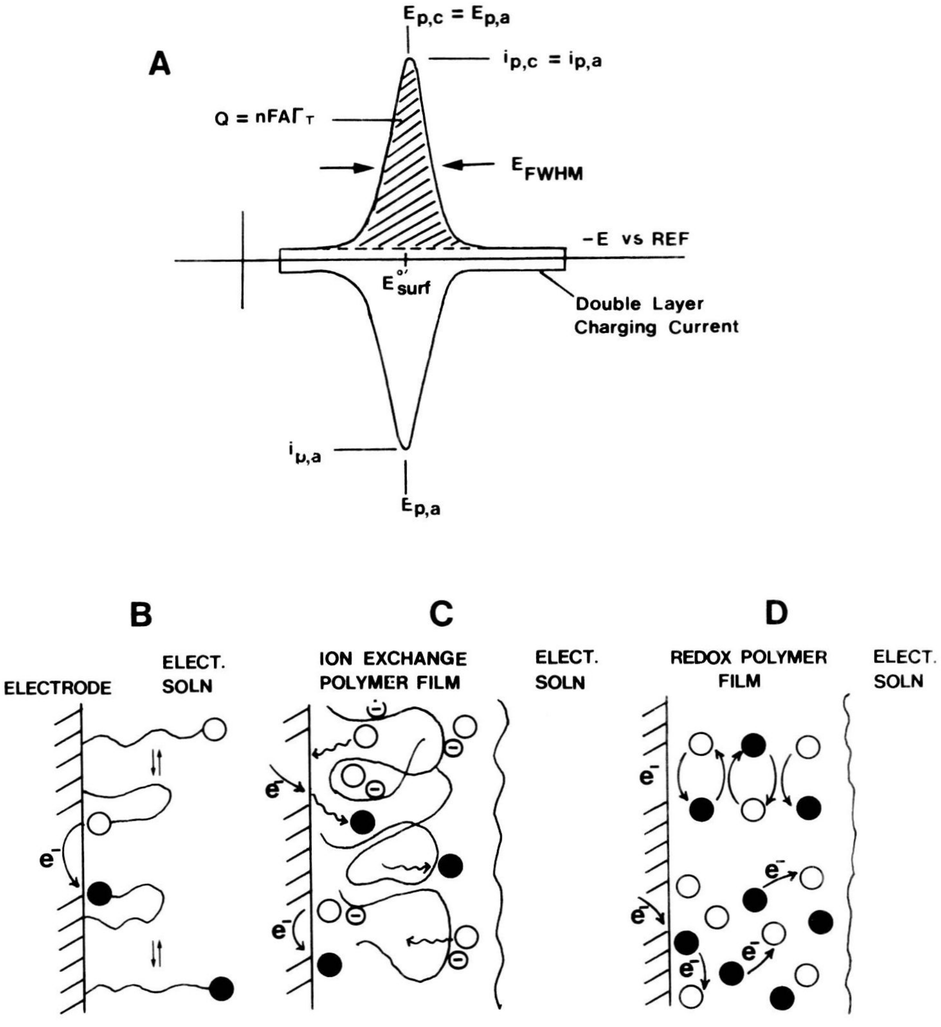

Figure 1.2. Curve *A*, ideal reversible cyclic voltammetric wave of an immobilized redox layer, whether monolayer ($\Gamma_T \lesssim$ ca. $10^{-10}\,\mathrm{mol\,cm^{-2}}$) or multilayer ($\Gamma_T \gg 10^{-10}\,\mathrm{mol\,cm^{-2}}$); Curve *B*, schematic reduction of monolayers attached by insulating yet flexible molecular chain; Curves *C* and *D*, schematic reduction of multimonolayers of ion exchange and redox polymers.

formal potential E°_{surf}. Both monomolecular and multimolecular layer reactions have (at least) two parts: transport of the redox molecule within the immobilization matrix to the site of the electron-transfer reaction (whether contact collision with the electrode or some longer range electron exchange), and the electron-transfer step itself. For the monolayer case, transport is a microscopic issue related to the flexibility of the molecular immobilization apparatus as discussed above. For the multilayer case, transport is a more complicated issue since the multiple monolayers of Ox and Red are held within a macroscopically thick film on the electrode. Ox and Red may be confined within the film but free to diffuse within it to the electrode–film interface (Fig. 1.2*C*). This is the case for ion-exchanged electroactive films (Section 1.4.2). Alternatively, if Ox and Red are also attached to the molecular framework (Sections 1.4.1 and 1.4.3) then their electron exchange with the electrode is indirect and depends on a succession of *electron self-exchanges* as shown in Fig. 1.2*D*.

In all of the cases in Fig. 1.2, understanding the electroactivity of the redox molecular layer involves (a) the thermodynamic characteristics of the donor–acceptor couple (i.e., what is E°_{surf} and is it similar to E°_{soln} of an analogous, nonimmobilized molecule) (16), (b) the kinetics of the electron-transfer step, and (c) the kinetics of transport of electrochemical charge (i.e., transport as in Fig. 1.2*C* or *D*) within the immobilized molecular layer.

The simplest immobilized redox layer undergoes a reversible reaction, that is, interlayer transport and electron transfers are fast on the experimental timescale (i.e., in cyclic voltammetry the potential sweep timescale, v volts/sec). In this case, the Ox/Red composition of the redox layer maintains equilibrium with the applied potential and is described by the Nernst equation at each E_{applied}. The observed current peak is symmetrical and the same whether observed in a positive or negative-going potential sweep, and for a reduction is given by (1, 5)

$$i = \frac{-4i_{\mathrm{p}} \exp[(n\mathscr{F}/RT)(E - E^\circ_{\mathrm{surf}})]}{\langle 1 + \exp[(n\mathscr{F}/RT)(E - E^\circ_{\mathrm{surf}})]\rangle^2} \tag{1.1}$$

where the current peak occurs at E°_{surf} and is

$$i_{\mathrm{p}} = \frac{(n\mathscr{F})^2 A \Gamma_T v}{4RT} \tag{1.2}$$

and Γ_T is total *electroactive coverage* (e.g., the sum of the mol cm^{-2} quantities of Ox and Red, $\Gamma_{\mathrm{Ox}} + \Gamma_{\mathrm{Red}}$), A is the electrode area, n is the number of electrons, and v is potential scan rate. The significant experimental observables are the proportionality between i_{p} and potential sweep rate v, equal peak potentials ($\Delta E_{\mathrm{p}} = 0$, see Fig. 1.2*A*), identical waveshapes for the cathodic and anodic current–potential curves, which are called *surface waves*, and the peak width $E_{\mathrm{fwhm}} = 90.6/n$ mV (where fwhm = full width at half-maximum).

Examining the proportionality between i_{p} and v is straightforward and, when