

APPLICATIONS OF CHEMICALLY MODIFIED ELECTRODES

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Abstract

An overview is presented of the major areas of applications of chemically modified electrodes. No attempt has been made to comprehensively review the literature. Rather, successful examples from each area have been used to illustrate the principles involved.

Introduction

Chemists working with electrodes used to spend a great deal of time cleaning their electrodes to obtain clean surfaces. Things seemed to have turned topsy — turvy in the recent past, where the effort has been to put on almost anything that sticks on to the electrode, and thereby modify its surface. The purpose of this of course is that the electrode will now display properties related to the molecular properties of the surface layer. One can think in terms of electrodes which are "tailor-made" for specific purposes. The major areas of applications of modified electrodes are,

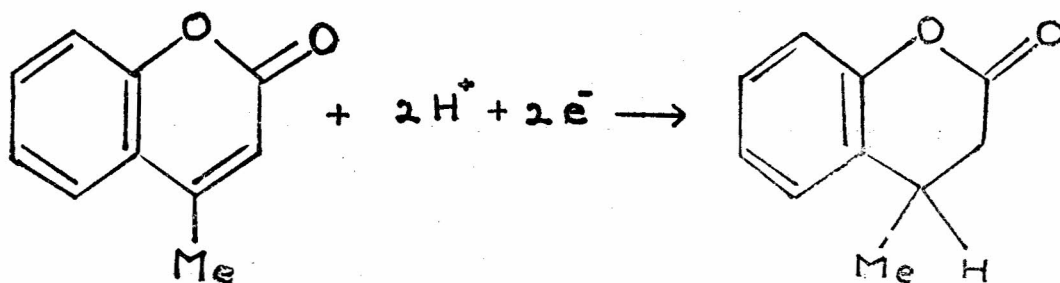
1. Asymmetric Synthesis
2. Electrocatalysis
3. Analysis
4. Solar Energy Conversion

We will now consider each of these in turn.

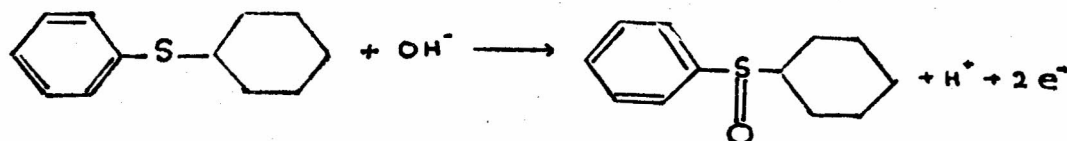
Asymmetric Synthesis

Although it had been known for a long time that substances dissolved in an electrolyte solution could adsorb on an electrode and change the characteristics of that electrode, use of this phenomenon to deliberately modify the course of an electrode reaction is a relatively recent event. The first asymmetric synthesis using a mercury electrode modified by an adsorbed layer of a chiral alkaloid was reported in 1970 (Grimshaw, et.al., 1970).

4-Methyl coumarin was reduced at a mercury electrode in an electrolyte solution containing the chiral alkaloid, sparteine.



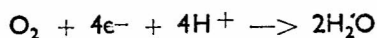
The yield of the product was 3.5% and it contained an enantiomeric excess of the R(+) isomer of 17%. In this case the chiral alkaloid is adsorbed on mercury at the interface, and the reduction of the substrate takes place within a chiral environment, resulting in an optically active product. Dramatic improvements in the chemical yield and the enantiomeric excess are achievable by modifying the electrode surface permanently by attaching a chiral molecule to it. Nonaka's (1983, 1983a) group in Japan prepared a chiral electrode by coating poly-L-valine (M.W. 2000) on Carbon, with which 4-methyl coumarin was reduced to its dihydro derivative in a yield of 8% containing an enantiomeric excess of the S(-) isomer of 43%. Similarly, using a poly-valine coated platinum electrode, asymmetric induction in the oxidation of phenyl cyclohexyl sulphide was observed.



Chemical yield = 34%
 enantiomeric excess (-) = 28%

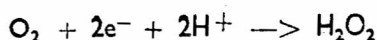
Electrocatalysis

The possibility of electrocatalysing useful reactions is one of the driving forces for research in modified electrodes. The reduction of oxygen to water,



is crucial to fuel cell technology.

The need here is for a cheap electrode that will produce an useful current density at the reversible potential for the reaction (1.23 V vs. NHE). Most of the large number of macrocyclic transition metal complexes that have been studied as electrocatalysts function only at potentials quite negative to the reversible value and in addition are capable only of a two-electron reduction of oxygen to hydrogen peroxide.



In an elegant bit of chemistry, Collman (1980) reasoned that a four electron reduction of dioxygen to water could be best achieved by a binucleating ligand capable of holding two metal centres in a suitable geometry so that they may jointly bind a dioxygen molecule. Each metal centre would then transfer two electrons to effect a four electron reduction. Experiments with a series of "face to face" dicobalt porphyrins showed that the desired reaction took place on a graphite electrode modified by deposition of a "face-to-face" porphyrin where the two porphyrins faces were separated by four atoms. (Fig. 1)

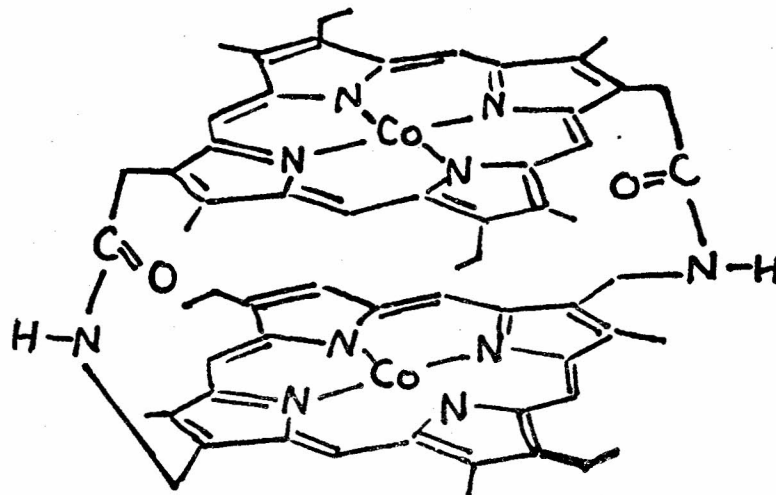
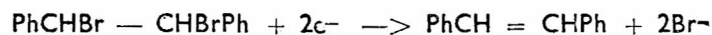


Fig. 1—Face to Face Dicobalt Porphyrin.

The reduction of vicinal dihalides to alkenes can be carried out electrochemically.



For example, the above reaction takes place on a bare platinum electrode at -2.02 V (vs. $\text{Ag}/0.1$ M AgNO_3). The process is made more energy efficient and takes place, at -1.6 V if platinum electrode is modified by a surface layer of poly-paranitro styrene (Miller et. al. 1980).

It is relevant at this stage, to consider the mode of action of such electrodes where the surface modifying layer is a polymer containing redox centres. The basic mechanism of electron transport in these layers is a site-to-site electron hop, where each redox site is in turn reduced and oxidised. (Fig. 2)

The substrate can react with the electron either at the polymer/electrolyte solution interface (as shown) or within the layer if it diffuses into it. High catalytic efficiencies are possible with these systems because of the high

local concentration of active sites arranged 3-dimensionally as in homogeneous catalysis. In addition they have the advantage of heter-ogeneous catalysts in providing easy separation of products. (Andreux, 1986).

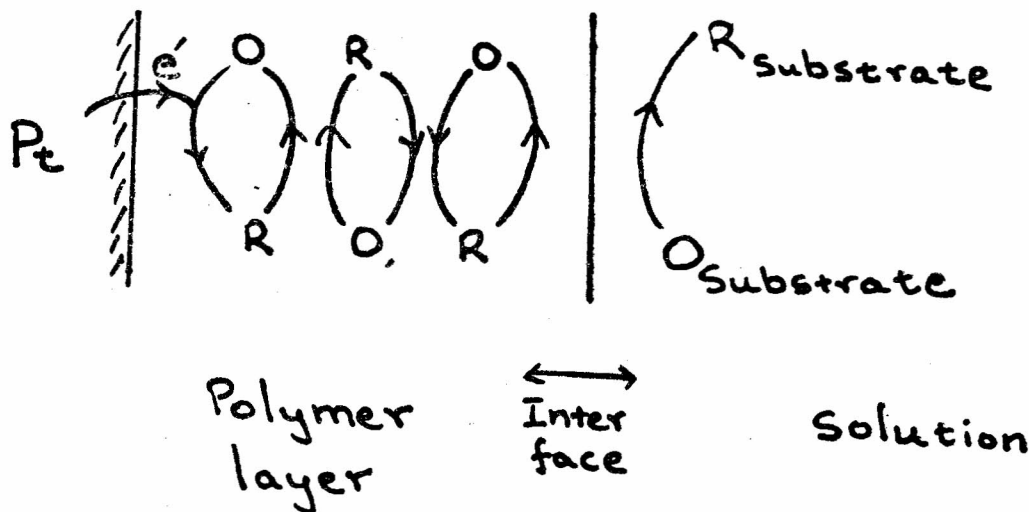


Fig 2— Mediated Electron Transfer in a Polymer Modified Electrode containing Redox Groups.

Analysis

There are numerous potential analytical applications of modified electrodes particularly in Medicine and Biotechnology. The central problem here is to achieve fast, reversible electron transfer to redox enzymes. This is generally difficult to achieve due to the incompatibility of the metal electrode surface with proteins and also the inaccessibility of the redox site which is buried within the protein structure. The conventional approach to this problem is to use mediated electron transfer via a small molecule that can shuttle back and forth between the electrode and the enzyme. There are two possible variations on this theme. One is to attach electron relays to the enzyme. Thus Degani and Heller (1987, 1988) observed a glucose concentration dependent current with a platinum electrode (when the electrolyte contained glucose oxidase) that had been modified by the attachment of ferrocenoyl groups.

The effectiveness of the ferrocene/ferricenium couple in electron shuttling had been shown by Hill et. al (1986). Based on this, a commercial graphite modified electrode utilizing the ferrocene/ferricenium redox couple mediated electron transfer, is now available. The device enables diabetics to take an instant blood glucose level reading from a single drop of blood (Chemistry and Industry, 1988, 571).

The other variation is to modify the electrode with a polypeptide so that it is compatible with enzymes, and to attach a "mobile arm" to the polypeptide. Such electrodes have been prepared and their physico-chemical properties including reversible conformational changes have been reported (Abeysekera & Grimshaw 1987, Abeysekera et. al. 1989). Electron transfer to enzymic or non-enzymic substrates using these electrodes have not yet been reported.

A particularly interesting application of modified electrodes in analysis, is their use as preconcentrating surfaces. The basic concept here is that the analyte is concentrated on the electrode by chemical reactions with the groups attached to the electrode, and then measured by the electrochemical response to a potential step or sweep. The chemical (preconcentration) step in such an electrode should be selective or the analyte should produce a distinctive electrochemical response. Further, the surface should not readily saturate and there should be a good signal to noise ratio. With such an electrode it is possible to analyse extremely dilute solutions. For example silver solutions of only 10^{-11} M have been analysed by using a carbon electrode modified with molecules containing terminal amino groups. (Cheek and Nelson 1978). The Ag(I) ion is preconcentrated by coordination to the $-\text{NH}_2$ groups. (Fig. 3)

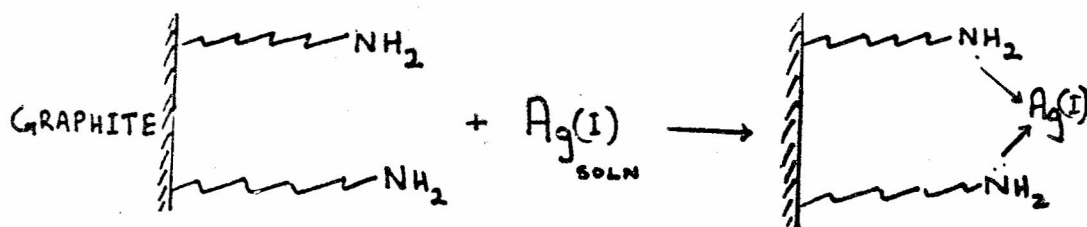


Fig. 3—Preconcentration of silver ions by modified electrode.

Solar Energy Conversion

This is the final category of applications of chemically modified electrodes that would be considered in this article. There are many approaches to the problem of the utilization of solar energy. The use of low band gap semiconductors such as n-Si as a photosensitized anode in a solar cell is plagued by the problem of corrosion.

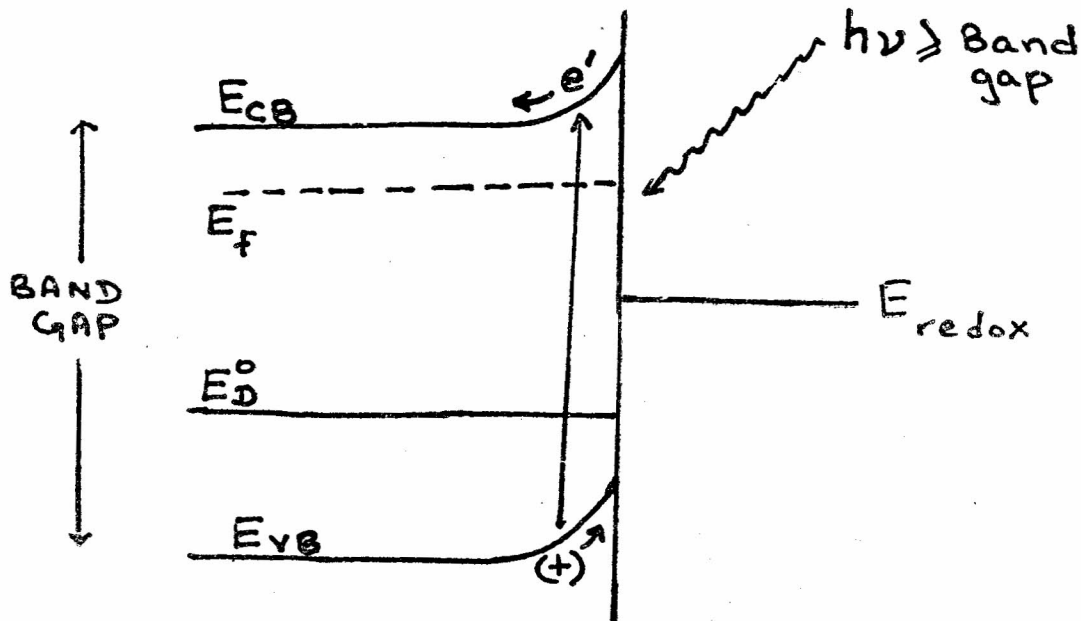


Fig. 4—Energetics of Photoanodic corrosion protection.

The energetics of the process is illustrated in Fig. 4. Photogenerated holes migrate upto the surface of the semiconductor and oxidise the semiconductor because the formal oxidation potential for decomposition (E_D^0) is more negative than the valence band potential (E_{VB}). If the surface is modified by attaching to it a fast redox couple whose potential is more negative than (E_{VB}), then the modifier can oxidise in preference to the surface, and thereby protect it.

It is necessary that the redox potential of the modifier (E_{redox}) be more negative than (E_D^0), otherwise the modifier could oxidise the semiconductor surface. Wrighton (1979) has demonstrated a dramatic improvement in the stability of n-Si when it is derivatised with Ferrocene species. The derivatisation chemistry is as shown in fig. 5.

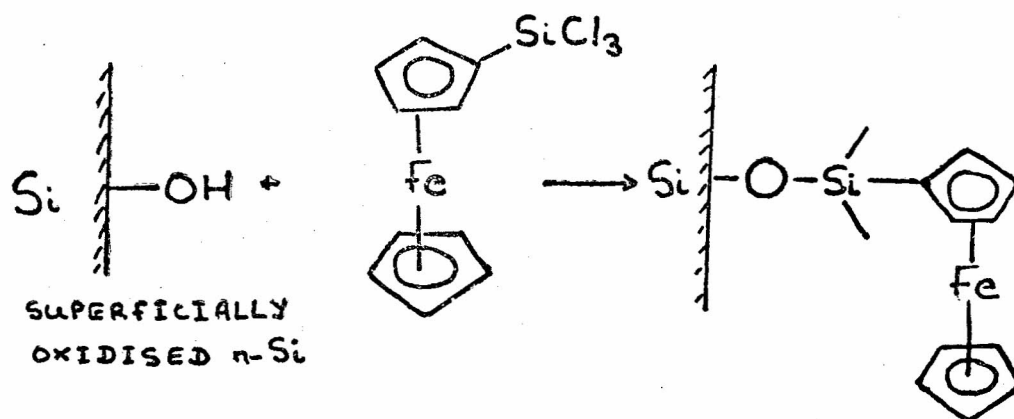


Fig. 5—Modification of silicon photoelectrode with ferrocene.

Obviously, to get a continuous photo current, there must be another redox couple in solution to bring the oxidised modifier back to the reduced state. In the Wrighton experiment, this was the ferricyanate ion. This electrode then achieves the photoelectro-chemical oxidation of $Fe^{2+} \rightarrow Fe^{3+}$ in solution. The possible extension to other redox processes in solution is quite clear. Thus, modified semiconductor electrodes, in addition to being stable to corrosion afford the possibility of carrying out photoelectrochemical transformations of species in solution.

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