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Chemically and physically modified electrodes: some new developments*

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In this review some new developments of physically and chemically modified electrodes are discussed. An overview is given for the principal routes of chemical modification and the characterization of the so-obtained electrodes. Special attention is paid to polymer modification of electrodes. The review ends with the presentation of some striking examples of applications in the field of analysis and synthesis. Some possible future developments are also suggested.

1. Introduction

The aim of this review is to draw attention to some new developments in the field of both chemically and physically modified eletrodes. For the first type of modification, the field up to 1984, is covered in an exhaustive and authorative way by Murray [1]. To make the present review consistent, it was necessary to incorporate the most significant older literature. Limited attention is paid to newer developments and the choice of these is the author's. The same applies for the physically modified electrodes. These comprise not only physical changes in the texture of the electrode material, but also changes in the space-time domain of active species near the electrode, so influencing the course of an electrode reaction.

Briefly, the reasons for modification will be summarized. Firstly, there is not only a need for more reactive and stable electrode materials: more selective materials are also needed, as is the case in (bio-)chemical catalysis. A very interesting approach in this respect is the immobilization of a homogeneous catalyst on a porous support; porous, because of a much higher active surface area. It is clear that, in principle, such an approach is also applicable to the field of electrochemical catalysis (electrocatalysis), although here the support should be electronically conductive. So the usual supports in chemical catalysis, such as alumina and silica, must be excluded and replaced by metals and such materials as porous carbon, etc.

Secondly, there is a definite need for extension of the arsenal of catalytically active electrode materials, not only for carrying out reductions but, even more, for oxidations. In the latter case only carbon, noble metals, some oxides — such as lead dioxide — and conductive ceramics are available.

Thirdly, as in chemical catalysis, there is in electrocatalysis a growing interest in designing these materials, i.e. to tailor an electrode so that it exhibits the properties required for the reaction in mind. This means that one must also be able to define the qualifications for the reaction, and it is clear that methods, both electrochemical and spectrochemical (and others), must be available — and they are — to characterize these materials.

Moreover, immobilization of a catalytically active chemical should preferably mean that it also maintains its (electro-)chemical and physical properties in the immobilized state. If this can be realized, selection of the chemical can be made on the basis of known properties desired for the electrode reaction in mind. In this respect, the routes to immobilization of electrochemically reactive substances are of utmost importance. These routes can be grouped as chemisorption, covalent bonding and attaching a film by (electro-) chemical or physical deposition, routes that are described in a thorough way by Murray [1]. Because of this, such routes are only summarized in Table 1, and we make some brief remarks.

1. *Chemisorption*. This type of binding refers to irreversible adsorption, in which the interaction with the substrate material bears some resemblance to a covalent bond. Usually, the layer so created is of the (sub-) monolayer type and so rather vulnerable to erosion.

2. *Covalent bonding* supposes a substrate which is not only electronically conductive, but is also prepared in such a way that covalent bonding with the electrocatalytically active molecule is possible. Substrates like carbon and metal oxides are, by nature,

suitable for making bonds of the ester, ether and amide type. Modification with more than one monolayer is possible.

3. *Film deposition*. This modification route is the most promising because, if the procedure is carried out carefully, a film is less vulnerable than layers prepared by chemisorption or covalent bonding, since thicknesses equivalent to up to $\sim 10^5$ monolayers are possible. In most cases the material is polymeric, and either electronically or ionically conducting. Moreover, there are indications that homogeneously acting catalysts, covalently bonded to the polymeric backbone, can be arranged in such a way that stereospecificity, and even enantioselectivity, is becoming a possibility.

2. Electrocatalytic aspects

Modification of electrodes can meet higher demands for selectivity, both qualitatively and quantitatively but, moreover, offers a means to design electrodes capable of exhibiting desired electrocatalytic properties. However, one must keep in mind that electrocatalysis not only points to the electrode material (the electrocatalyst) itself, but that it is the interplay of the electrode material with the solvent, the electrolyte and the substrate which ultimately determines the course of the desired electrochemical reaction. That the environment (type of solvent, and type and concentration of electrolyte, and concentration of substrate) plays a decisive role will be illustrated later on. The reason why is simple: the electron transfer and part of the chemical reaction, mostly accompanying this transfer, occurs in, and is determined by, the electrochemical double layer. On the other hand, and looking at the electrode reaction itself, adsorption plays a crucial role in selectivity. And because adsorption is governed by the electrode material and the double layer as well as by the potential it is clear that, in order to have the most appropriate electrocatalyst, the study of the adsorption behaviour is essential in characterizing the electrode.

3. Characterization

Methods of characterizing the electrode material can be divided into electrochemical and spectrochemical methods.

3.1. *Electrochemical methods*

A *sine qua non* for each characterization is cyclovoltammetry, which can be considered as a fingerprint: it gives information about redox states fixed onto the electrode. If, for instance, an electroactive molecule (a reversible redox system) is covalently immobilized to approximately a monolayer, then, for ideal behaviour, the peak current, i_p, is proportional to the potential sweep rate, v (V s^{-1}). Moreover, in this case, the anodic and the cathodic peaks are each other's mirror image, i.e. $E_{pa} = E_{pc}$ and $i_{pa} = i_{pc}$; also, $E°$(surface)

has about the same value as $E°$(soln). In addition it is now very simple to derive, from the peak charge, the surface concentration (i.e. for a monolayer, as a rule of thumb, 10^{-10} mol cm^{-2}). AC voltammetry and differential pulse voltammetry are even more sensitive. Impedance plots, especially complex-plane plots, are helpful too, particularly in analysing the behaviour of electronically conducting polymer films. However, it must be stated that most systems — and certainly polymeric films — do not conform to ideal behaviour, so that deviations from ideal expressions are the rule rather then the exception. Further, one must keep in mind that the net electrocatalytic activity of an electrode, modified or not, is not so much a question of presence but of accessibility of active sites. This point can be made clear with the following example [2].

Suppose an irreversible cathodic reduction has as the first rds a one-electron transfer, so that

$$i/i_1 = \{1 + (k_D/k)\}^{-1} \qquad (1)$$

with i_1 the limiting current density, k the heterogeneous rate constant, and k_D the mass-transfer rate constant. Now at $E_{1/2}$ and for N accessible active sites (case 1), $k = k_D$. For pN accessible active sites (case 2), however, the heterogeneous rate becomes proportional to pk, with k_D remaining constant. For case 1

$$k_D = k_0 \exp\left(-\alpha\, F\eta_1/RT\right) \qquad (2)$$

and for case 2

$$k_D = pk_0 \exp\left(-\alpha\, F\eta_2/RT\right) \qquad (3)$$

with $k_0 = k$ for $E = E_{eq}$, i.e. $\eta = 0$. From (2) and (3) follows

$$\eta_2 - \eta_1 = \Delta E_{1/2} = (RT/\alpha\, F) \ln p \qquad (4)$$

In other words: a ten-fold increase of the number of accessible, active sites cause a shift in the half-wave potential equal to the Tafel slope. A system illustrating this point is dioxygen reduction with cobalt tetrasulphonato phthalocyanine. If irreversibly adsorbed onto pyrolytic graphite, its activity is less than if it is built-in in an electronically conducting film of polypyrrole; in the latter case the overpotential is decreased by more than 200 mV [2].

3.2. *Spectrochemical and other methods*

All electrochemical methods for characterization are, by nature, *in situ* methods. They often will not produce universal clarification. Spectrochemical methods are especially worth considering because they can give extra information about surface composition and structure not obtainable from electrochemical methods. Spectral methods partly allow *in situ* measurements: transmission spectroscopy at optically transparent electrodes (SnO_2, Pt, Au, Ni on glass), reflectance spectroscopy (VIS, UV, IR), ellipsometry, interferometry, surface enhanced Raman spectroscopy (SERS), etc. The informative value is mostly supplementary. Methods like XPS, AES, SEM, SIMS, and others, are by nature *ex situ* methods: *post mortem* analysis results
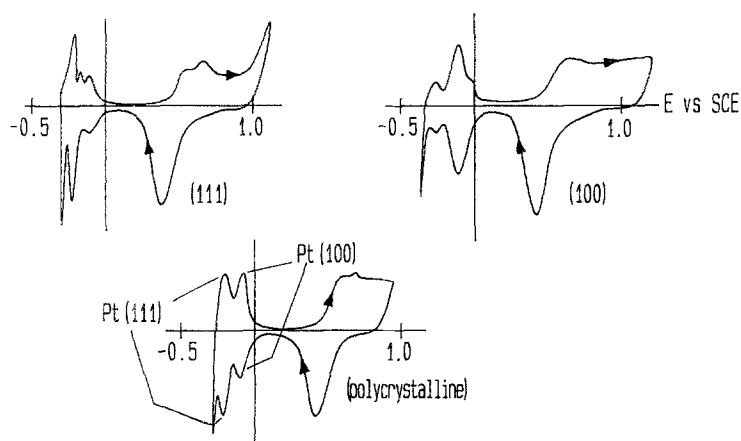
Fig. 1. Cyclovoltammograms for several types of platinum in 1 M H_2SO_4 with a potential scan rate of $10 \, mV \, s^{-1}$. Continuous scanning results in a surface lattice structure with predominant Pt(100); own results.

must then be compared with results obtained before the electrochemical experiment.

Some other possibilities of characterizing the electrode surface are by radio-labelling, photoacoustics and measurement of the contact angle (which is important because hydrophobicity also influences the course of an electrode reaction).

4. Physical modification

In most cases chemical modification can provide the solution for an activity or selectivity problem. However, the possibility of physical modification has also to be considered, if only because of the implicit enhanced stability. In principle, there are two approaches;

— physcial modification of the electrode surface;
— physical modification of the immediate environment of the electrode.

4.1. Physical surface modification

In general, there are two effects, in most cases occurring together. By roughening the electrode surface the surface area is increased so that there is a real enhancement of the number of accessible active sites and, therefore, of activity (as is the case in platinizing). Moreover, a change, both in type of active sites and in the way they are distributed over the surface, also occurs; i.e. the selectivity changes.

A change in the type of active sites can, in some cases, also be accomplished by cycling the potential of the electrode or by recrystallization. How the surface crystal structure of platinum can be transformed from a polycrystalline lattice structure (a mix of Pt(100) and Pt(111)) to a structure with (100)-type preferred orientation) is illustrated in Fig. 1. As the lattice structure determines the adlattice structure for adsorption of reagent, intermediates, etc., it is clear that in this way selectivity is also affected. Examples for this selectivity change are the oxidation of methanol and the reduction of oxygen [3, 4].

Another type of 'physical modification' involves physical adsorption. Though here the adsorption forces are rather weak, the adsorption situation can be kept stable if, for example we make use of a supporting electrolyte of which the cation is pronouncedly hydro-

phobic. In this case (the cation adsorbed onto a cathode) hydrolysis, as an intermediate chemical step in a reduction reaction, can be more or less inhibited in favour of another chemical step, let us say a dimerization reaction. The cathodic hydrodimerization of acrylonitrile to adiponitrile is a well-known example in organic electrochemistry.

4.2. Physical environment modification

Another type of 'physical modification' involves transforming the space–time relations near the electrode by making use of well-chosen electrochemical engineering (reactor design) principles. An electrode reaction not only involves electron transfer but also chemical reaction(s), preceding, in between, or following electron transfer. As these chemical reactions take place in a reaction layer adjacent to the electrode and because the concentrations of the participating species vary with the convection conditions, it is evident that different reactor designs can cause different reaction products. A striking example is the electrochemical methoxylation of furan [5], consisting of an electron-transfer step

$$2 \, Br^- \longrightarrow Br_2 + 2 \, e^- \qquad (5)$$
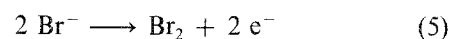
followed by a chemical step

$$(6)$$

Using the bipolar capillary gap cell, the bipolar pump cell, or the bipolar trickle tower cell, gives rise to a different ratio and extent of byproducts, i.e. selectively is greatly influenced by reactor design. Well-known in this context is that results obtained at micro-electrodes cannot simply be translated to macro-scale situations; the same applies for translating results obtained under batch conditions to continuous conditions.

5. Chemical modification

Though the possibilities of physical modification must not be overlooked, chemical modification offers a

Table 1. Possible routes for chemical modification

Type	Method	Type of binding	Properties
I. (Sub)monolayer			
1. Ad-Me-atoms	Dipping	Irreversible chemisorption	Spill-over catalysis with under-potential deposited (UPD) metal atom (sub-monolayer)
2. Molecules	(a) Dipping	Irreversible chemisorption	Mostly monolayer; also e^--hopping mechanism; symmetrical CV
	(b) Chemical reaction with pretreated substrate eld	Covalent	Mostly monolayer; also e^--hopping mechanism; symmetrical CV
II. Multilayer			
1. Monomeric units	(a) Droplet evaporation, Painting	Cohesion and adhesion forces	Ion- or electron-conducting with e^--hopping; mostly porous
	(b) Chemical vapour deposition, Plasma spraying	Cohesion and adhesion forces	Ion- or electron-conducting with e^--hopping; mostly porous
2. Monomeric and oligomeric units	Chemical reaction with pre-treated substrate eld	Covalent	Conduction by electron hopping; mostly porous
3. Polymeric units	Electrochemical deposition	Cohesion and adhesion forces	Ion- or electron-conducting with e^--hopping; sometimes porous
III. Built-in systems in polymers	Simultaneous electro-chemical deposition	Cohesion and adhesion forces	Ion- or electron-conducting; sometimes porous

definite and fruitful approach to the need of producing better electrocatalytic systems, as explained above. One of the most remarkable inventions in this respect is that of the dimensionally stable anode (DSA) by Beer in the early sixties [6].

In general, chemical modification can be accomplished in several ways: droplet evaporation, dipping, (plasma) spraying, (electro-)chemical vapour deposition, (electro-)chemical deposition, etc. The result of one of these acts is the formation of a (sub-)monolayer, or a multilayer; a special case of the latter is the electron- or ion-conducting polymer film.

Fig. 2. Cathodic reduction of dioxygen, 2.4×10^{-4} M, at RDE-Au (111) with UPD-Pb in 0.5 M $HClO_4$; (———) with 6×10^{-4} M $Pb(ClO_4)_2$, (———) without $Pb(ClO_4)_2$ [7].

The type of attachment, c.q. binding, is not only a consequence of the method chosen (dipping, etc.) but also of the type of substrate material used: metal (oxide), semiconductor, carbon, graphite, etc. Some methods result in a cohesion type of attachment (e.g. droplet evaporation, spraying, electrochemical deposition); others in irreversible adsorption (e.g. dipping) or in a covalent type of binding via a chemical reaction. The thickness of the layer, as well as the type of attachment, is of utmost importance for the stability of the modified electrode.

We confine ourselves here to a short overview of the principle routes for chemical modification (for more details see [1] and Table 1).

5.1. Principal routes

The significance of *under-potential deposition (UPD)* of metal atoms can best be illustrated by an example [7]. The electrocatalysis of the reduction of dioxygen in a 0.5 M $HClO_4$ solution at a gold (111) electrode is much enhanced by the addition of a dilute $Pb(ClO_4)_2$ solution (6×10^{-4} M) (see Fig. 2). One supposes that dioxygen is bridge-adsorbed onto a gold atom and a lead atom, forming a bimetallic complex and so enhancing reactivity.

Irreversible adsorption of transition metal organic complexes, such as tetra-sulphonato cobalt phthalocyanine on pyrolytic graphite, gives a modified electrode, suited to the reduction of dioxygen in alkaline medium [8].
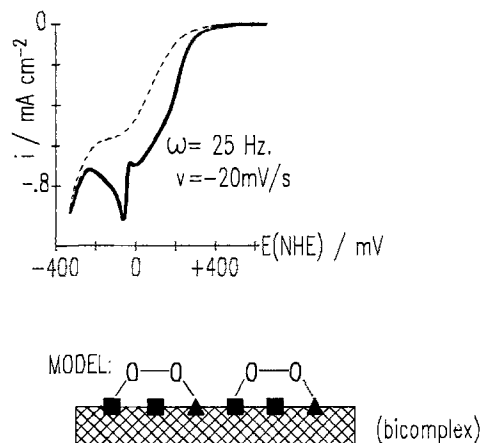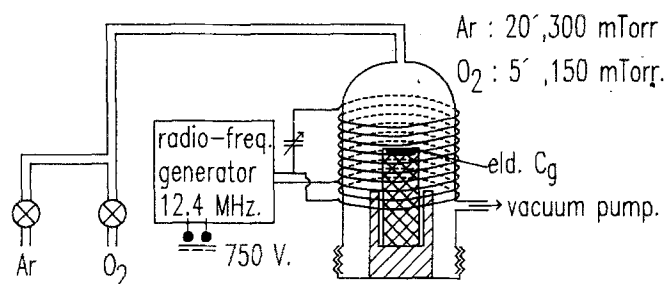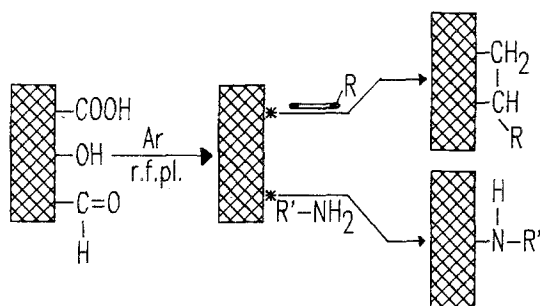
Covalent modification via activated(∗) surface.

Fig. 3. Chemical modification with vinyl or amine compounds at a highly, by rf-Ar plasma, activated carbon surface. R is a functional group.

Covalent binding (entries I.2(b) and II.2 in Table 1) is a suitable method for modifying an electrode, though the monolayer system is rather vulnerable. Because the modification procedure requires a chemical reaction with the substrate electrode, its surface must first be pretreated.

The surface of a metal (Pt, Pb, Ni, etc.) is first transformed into an oxide or a hydroxide; if carbon or graphite is used, its surface has to be oxidized in such a way that it preferently exposes hydroxyl or carboxylic groups. Such functional groups can be generated by chemical oxidation (by nitric acid, for example) by

thermal oxidative treatment, or by radio-frequency plasma treatment (see Fig. 3). If an argon plasma is used, it is even possible to achieve a highly activated electrode surface [9].

5.1.1. Metal (hydr)oxides. A metal, even a noble metal like platinum, is often covered with a hydroxide layer or an oxide layer. It is then possible, with the aid of a bridge molecule, e.g. an organosilane, X_3Si-R (where X is a halogen and R is a functional group or even an electrocatalytic group), to introduce electrocatalytic functionalities. Under anhydrous conditions an ether bond can be formed, giving rise to a monolayer or even to dimeric or oligomeric layers (see Fig. 4) [1].

Hydroxyl groups also offer the possibility of introducing electrocatalytic functionalities via an ester bond.

5.1.2. Carbons (glassy carbon, (pyrolytic) graphite). Carbon, as glassy carbon or (pyrolytic) graphite, offers

R = functional group.
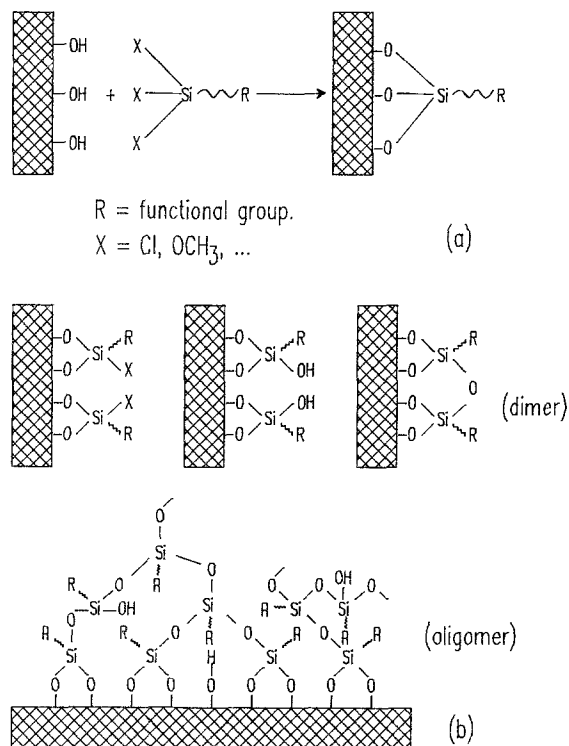X = Cl, OCH₃, ...

(a)

(dimer)

(oligomer)

(b)

Fig. 4. Formation of a monolayer (a) or an oligomeric structure (b), making use of organosilanes as bridge molecules.
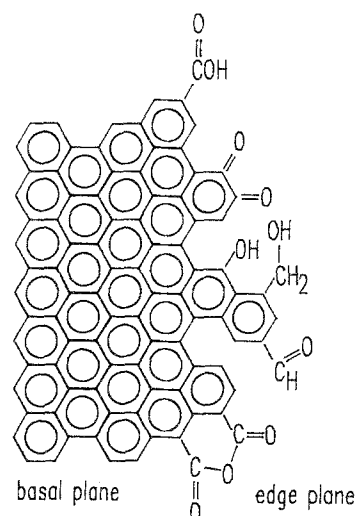

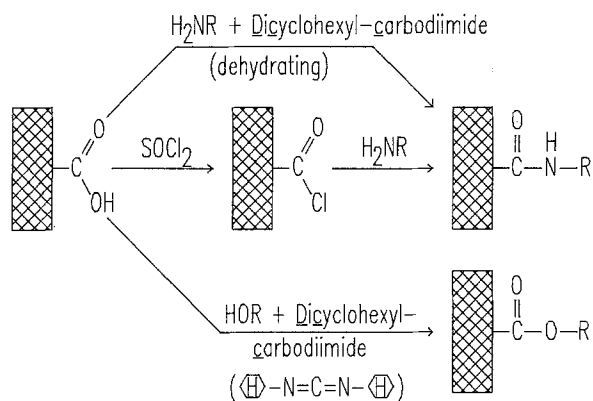Fig. 5. Functionalities at the edge plane of pyrolytic graphite.

Fig. 6. Making a peptide or an ester bond by using sulphonyl chloride and/or the dehydrating agent DCC (dicyclohexylcarbodiimide, $\langle H \rangle - N = C = N - \langle H \rangle$).
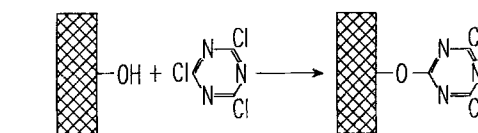

Fig. 7. Attaching of the bridge molecule cyanuric chloride at a pretreated carbon surface.

still more functionalities; those at the edge plane of pyrolytic graphite are shown in Fig. 5. As can be seen, not only groups like hydroxyl or carbonyl, but also carboxyl, quinone, lactone and acid anhydride groups are present. It is even possible to carry out the oxidation in such a way that preferred functional groups are also formed. This oxidation can be performed chemically, but also by means of a rf plasma treatment [9], so that it is possible even to introduce amide, nitro, bromide and other groups. This offers many bonding possibilities, including the strong peptide bond. How this can be accomplished is comprehensively explained in the earlier review by Murray [1]. Here we only show how dehydration in the case of a peptide or an ester bond can be carried out (Fig. 6).

Another bridge molecule is cyanuric chloride [10]: an ether bond is formed and the catalyst can be attached at the nitrogen atoms (see Fig. 7).

5.2. Polymer modification [11]

Modification of an electrode with an electron- and/or ion-conducting polymer layer is most promising both because of its versatility (see also Section 5.3) and its better stability. As a typical example of this kind of modification polypyrrole (PPy) must be mentioned, although other types like polythiophene, polyaniline, etc., are also of interest. In this review only a short overview of the polypyrrole modified electrode is given.
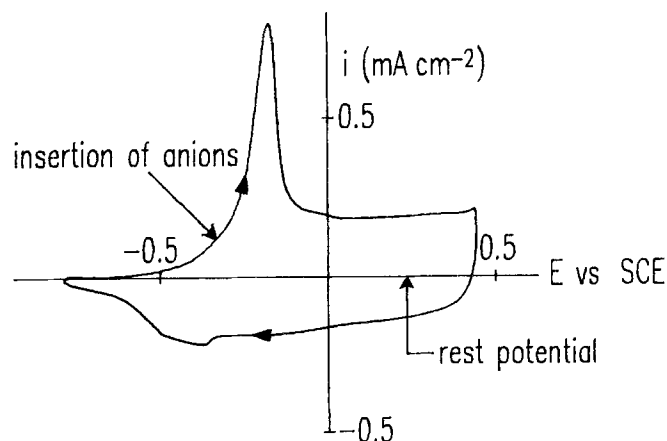
5.2.1. Preparation. Noble metals, such as platinum, or carbon (glassy carbon, pyrolytic graphite) are usually used as substrate electrode material. The anodic polymerization can be carried out in non-aqueous solvents such as acetonitrile (AN), dimethylformamide (DMF), but also in mixtures of these solvents with water, or even water itself. The type of electrolyte (especially the anion) plays a crucial role: perchlorate, tetrafluoroborate and p-toluenesulphonate are most commonly used in concentrations up to 0.1 M. The pyrrole concentration can also rise to 0.1 M. Both galvanostatic $(0.1 < i < 5\,\mathrm{mA\,cm^{-2}})$ and potentiostatic deposition (potential up to 1.1 V against SSCE, the sodium saturated calomel electrode with reference value 0.236 V against NHE) are in use. A typical cyclovoltammogram of a PPy layer is shown in Fig. 8. From this cyclovoltammogram it follows that insertion of BF_4^- anions starts at $-0.5\,\mathrm{V}$ against SSCE; from that potential onwards to higher potentials the conductivity of the film increases rapidly. At higher potentials, say from $+1.0\,\mathrm{V}$ onwards, and depending on polymerization conditions, the film becomes irreversibly oxidized. To understand this behaviour, something must be said about the mechanism of polymerization and that of charge transport.

5.2.2. Mechanism of polymerization. There is now common understanding about the mechanism of polymerization of pyrrole. Generally, one supposes the formation of a radical cation, followed by α,α-dimerization with a second radical (or by a neutral monomer), and deprotonation. Then, the same sequence is repeated until termination occurs, for instance with a water molecule as scavenger. For the polymerization, two electrons per monomer unit ($n = 2$) are necessary; see (7). Though the degree of polymerization is not known exactly, generally, a degree > 10 is supposed.

Fig. 8. Cyclovoltammogram of a 0.2 μm PPy-layer on platinum in 0.1 M Bu_4N BF_4/acetonitrile; $v = 20\,\mathrm{mV\,s^{-1}}$.

(7)
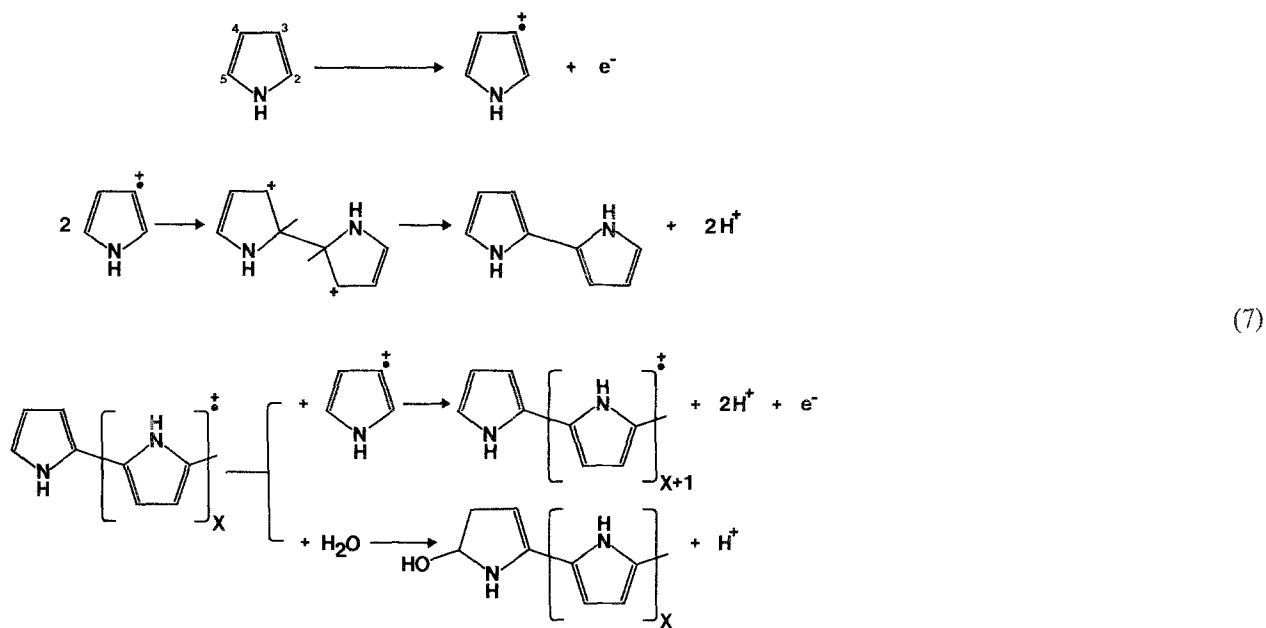
5.2.3. Mechanism of charging.

As proven by esr, charge transport in systems with non-degenerate ground states, such as polypyrrole and polythiophene, is, in general, spinless; moreover, interchain conduction is demonstrated. It is evident that polaron (radical cation) and soliton (cation) conduction do not occur. The most probable conduction mechanism therefore is by bipolarons (dications): see (8)

$(A^{\overline{\bullet}} =$ acceptor radical anion: "dopant")

(8)
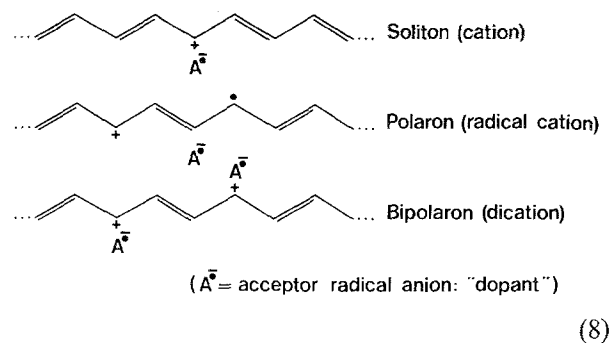
This means, because of the condition of neutrality, that anions must be inserted into the film. The type of anion is rather important for both the level of conduction and the stability of the film. One monovalent anion is necessary for every 2 to 4 pyrrole molecules. If we assume a degree of insertion of 0.25 (1 anion per 4 pyrrole units), then $n = 2.25$. Layer thicknesses are from 0.01 to 100 μm. As a rule of thumb, and assuming a high degree of polymerization with a density of 1.5 g cm^{-3}, the electrochemical equivalent and the layer thickness can be calculated as 0.40 mg C^{-1} and 2.75 μm C^{-1} cm^{-2}, respectively. Self-doping [12] seems promising; however, cation movement is now substituted for anion movement.

5.2.4. Conductivity.

Conductivity in a polymer can be based on an extensively delocalized electronic system, as described above for polypyrrole, but also on a redox conduction mechanism for polymer systems, mentioned in section 5.3 (see Figs. 9 and 10).

Although the level of conductivity is dependent on the type of polymer and the method of preparation (in particular the type of anion inserted in the potential range -0.4 V $< E < +0.8$ V against SSCE), such a polymer has a conductivity in the range of 10^2–10^3 ohm^{-1} cm^{-1} (compared with neutral polymer: $E < -0.4$ V against SSCE, 10^{-4}–10^{-8} ohm^{-1} cm^{-1}, and with metals: 10^5–10^6 ohm^{-1} cm^{-1}). The conductivity greatly depends on the degree of planarity: N-substituted PPy, for example, lacks planarity, as a result of which the specific conductivity is lowered by some four orders of magnitude [13].

5.2.5. Electrocatalytic activity.

There are examples in the literature showing electrocatalytic activity of a pure PPy-film. For example, for the cathodic reduction of dioxygen the selectivity for the reduction to water over that to hydroperoxide is markedly enhanced compared to the reduction at a bare platinum electrode [14]. Probably this is not as much a consequence of the intrinsic catalytic activity, but more likely
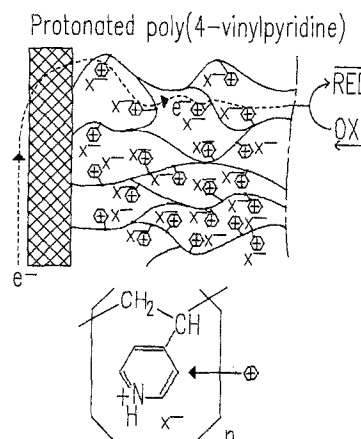

Fig. 9. Redox polymer electrode with protonated poly(4-vinyl-pyridine) as polymer matrix and X$^-$ = CoTSPc^{4-} as counter-ion/redox centre.

$-C-C-C-C- =$

$+ \bullet = Ru^{\pi}(edta)(OH_2)$, with, in soln.:

$E_p = -0.22$ V

i_a

$-0.2 \quad 0 \quad +0.2 \quad$ V vs SCE

C_p

now immobilized:

$E_p = -0.1$ V

i_a

$-0.2 \quad 0 \quad +0.2 \quad$ V vs SCE

C_p

after 25' :

$E_p = +0.18$ V

i_a

cross-linking:

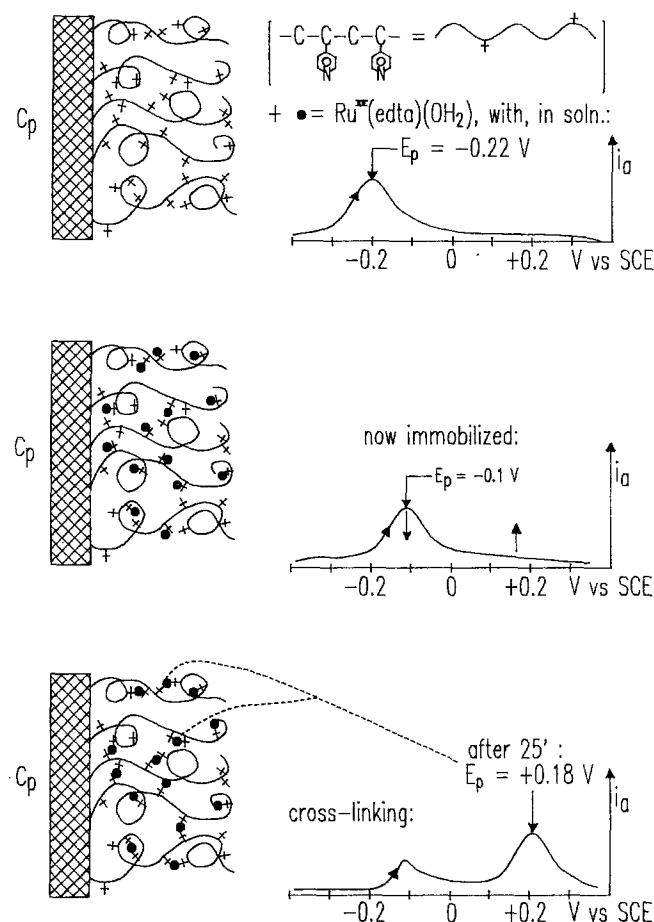$-0.2 \quad 0 \quad +0.2 \quad$ V vs SCE

Fig. 10. Immobilized $Ru^{II}(edta)(OH_2)$ redox complex at a pyrolytic graphite (Cp) electrode, modified with poly(4-vinylpyridine).

caused by a more favoured concentration ratio of intermediates at the Pt-PPy interface.

A more promising way to both activity and selectivity is the copolymerization of pyrrole with N-substituted pyrroles in such a way that the incorporation of those N-substituted pyrroles, carrying a catalytic centre (for example a ferrocene derivative), does not decrease conductivity too much. This means that the incorporation must occur in a regular way with the unsubstituted pyrrole units being in a majority [15]. But most promising seems to be the building of electrocatalysts, both in the molecular dimension as in the form of colloidal particles (see also Section 5.2.6.).

5.3. Built-in electrocatalysts

Because of its electronically conducting properties, it is possible to build in electrocatalysts to the PPy-film, as mentioned in the preceding section. This can be accomplished in several ways:

(a) Particles, preferably smaller than 100 μm, but also molecules, can be built in during the polymerization procedure. In the case of particles, one must be aware of the fact that most of these are in more or less direct contact with the electrode, but covered with a thin polymer film. A number of examples can be quoted from the literature [16].

(b) A special form of incorporation is the insertion of electro-catalytically active molecules in their anionic form, so that they act at the same time as dopant in the

oxidized state of the polymer. An example is the insertion of Co-tetrasulphonatophthalocyanine, CoTSPc, where the tetrasulphonatophthalocyanine anion, $CoTSPc^{4-}$, acts simultaneously as a catalyst and a dopant [17].

(c) There is some evidence that enantioselectivity can be achieved by insertion of proper anions as outlined above. Another approach of enantioselectivity is to make use of the copolymerization principle as described in Section 5.2.5. Striking examples are still lacking, however. This may be caused by the fact that chiral anions or molecules are mostly rather bulky, so distorting the planarity of the polymeric backbone and thus severely reducing conductivity.

(d) Also, instead of electronic conductivity, use can be made of ionically conductive polymers, like Nafion or protonated poly(4-vinyl-pyridine), H^+ PVP. In this case electrocatalytically active molecules can be inserted as described under (b). In Fig. 9, the modification is carried out with H^+ PVP, an anion exchanger in its protonated form. $CoTSPc^{4-}$, for example, can be used as the counterion X^- [18].

(e) It is, however, also possible to make use of polymers with functional groups, like PVP, and attaching to the group a redox system. As an example, in Fig. 10 the redox system Ru^{II} (edta) (OH_2) is incorporated in the polymeric network [19]. In this case, even cross-linking can occur, giving rise to extra possibilities in the redox catalysis.
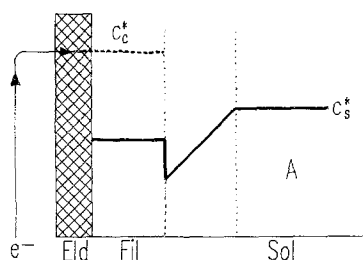
Fig. 11. Concentration profiles for S (——) and C(R) (– – –).

5.4. Concentration profiles in modified electrodes

If a stationary concentration profile in solution is assumed (and this assumption is realistic in sufficiently stirred solutions), then, for a cathodic reduction of a substrate molecule, S, to a product, P, at a redox catalyst, C, we have the following four steps

(i) $C(O) + e^- \rightarrow C(R)$

(ii) $C(R) + S \rightarrow P$

(iii) Diffusion of electrons through the film from the electrode–film interphase to the film–solution interphase, with the diffusion coefficient $D(e^-)$

(iv) Diffusion of S through the film in the reverse direction, with $D(S)$, and diffusion of P, direction solution, with $D(P)$.

If $D(S)$ and $D(e^-)$ are large and the reaction rate of step (ii) is small (rds), then we have concentration profiles for C(R) and S as depicted in Fig. 11 [20].

6. Some applications

In this section, a limited number of examples in the field of analysis, synthesis, biochemistry, etc., will be presented.
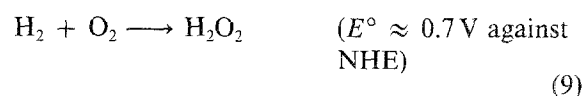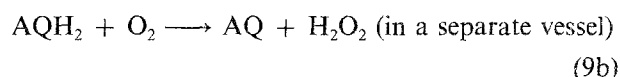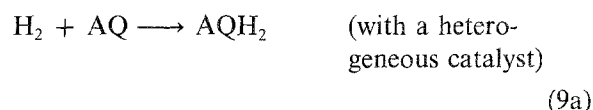
6.1. Analysis [21]

6.1.1. Salt bridge-free reference electrode for use in non-aqueous solvents [22]. A platinum wire, covered with a copolymer of pyrrole and ferrocene N-substituted pyrrole, as described in Section 5.2, can act as a reference electrode in non-aqueous solutions. This electrode must first be preconditioned at a fixed potential, $E = +0.38$ V against NHE, to a ferrocene/ferricinium ratio of 1 : 1. It is well known that the solvation activity coefficient for this redox system remains about the same, independent of the type of solvent involved. Therefore, this electrode must be

very suitable for comparing potentials and so, for instance, pH values in different solvents.
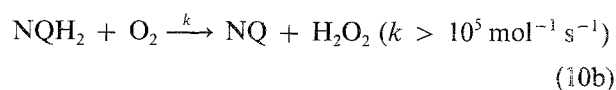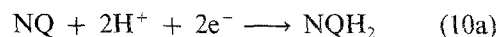
6.1.2. Glucose sensor in blood. In general, modification of, say, a platinum electrode with a redox enzyme such as glucose oxidase is possible [23], but in most cases electron transfer is problematic [24]. Glucose oxidase, GO, contains $FAD/FADH_2$, i.e. the flavine adenine dinucleotide redox enzyme, which in turn is protected by a polysaccharide membrane. To enhance electron transfer in the enzyme, this entity can be modified by specific incorporation of a ferrocene carboxylic acid derivative, as is shown in Fig. 12 [25]. However, such a modified GO is toxic, so that the sensor must be isolated from the blood. This can be done by using a diaphragm with pores smaller than 8 nm. The sensor can be coupled to an insulin delivery system, and so serve as a monitor. There is a lot of activity in this field (see, for example, [26]).

6.2. Synthesis

6.2.1. Synthesis of hydrogen peroxide. The industrial process consists of two steps

$$H_2 + AQ \longrightarrow AQH_2 \qquad \text{(with a hetero-geneous catalyst)} \tag{9a}$$

$$AQH_2 + O_2 \longrightarrow AQ + H_2O_2 \text{ (in a separate vessel)} \tag{9b}$$

$$H_2 + O_2 \longrightarrow H_2O_2 \qquad (E^\circ \approx 0.7\,\text{V against NHE}) \tag{9}$$

where AQ is anthraquinone. In principle, it is possible to carry out this synthesis as a one electrochemical step on a chemically modified electrode. In this case [27] naphthoquinone, as an electrocatalyst, is attached to the substrate electrode via silane as a bridge molecule (see Fig. 13). The reactions are

$$NQ + 2H^+ + 2e^- \longrightarrow NQH_2 \tag{10a}$$

$$NQH_2 + O_2 \xrightarrow{k} NQ + H_2O_2 \ (k > 10^5\,\text{mol}^{-1}\,\text{s}^{-1}) \tag{10b}$$

The system NQ/NQH_2 functions as a redox catalyst and the net reaction is as (9). This principle must be applicable to a great number of so-called indirect, organic electrosynthesis.
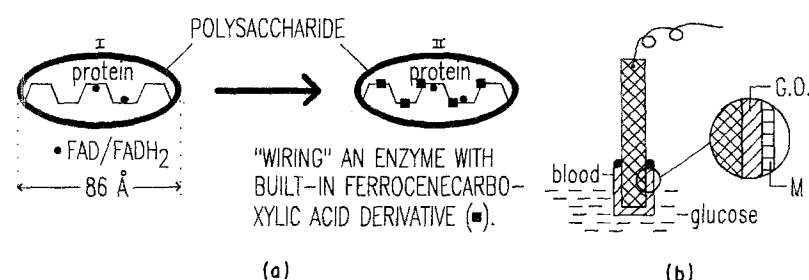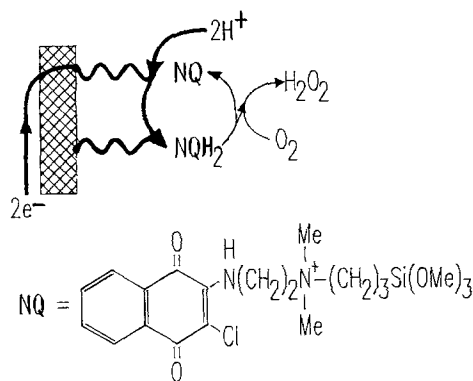

(a)

(b) Fig. 12. (a) Modified glucose oxidase; (b) sensor.

Fig. 13. Modified electrode for the reduction of dioxygen to hydrogenperoxide (silane bridged naphthoquinone).

Fig. 14. Preferential p-substitution of chlorine in anisole at a α-cyclodextrine modified graphite electrode.

6.2.2. *Stereo- and enantio-selective synthesis.* Though the results attained up to now are rather poor and even questionable, there are still possibilities. There is a claim [28] that preferential p-substitution of chlorine in anisole is possible with the aid of a graphite electrode, modified with α-cyclodextrine, as shown in Fig. 14.

6.3. *Bio- and photo-electrochemistry*

Especially in the field of bio- and photo-electrochemistry, chemical modification offers new possibilities. As to bioelectrochemistry there is much interest in enzyme modified electrodes, though there are still problems to overcome, one of them being deconformation of the enzyme structure if a potential is applied. In photo-electrochemistry, applications are numerous not only for decreasing photocorrosion but also in electrolysis, such as the photo-electrolytic splitting of water, as depicted in Fig. 15 [29]. However, in the latter case the products, hydrogen and oxygen, are not separated, and this is a technological disadvantage of the process.

7. **Concluding remarks**

Fundamental approaches would prove very helpful to applied electrocatalysis. Modified electrodes have already found application in electrosynthesis and electroanalysis. They are now on the brink of being introduced in energy conversion systems (fuel cells, water electrolysis) and bio- and photo-electrochemistry.
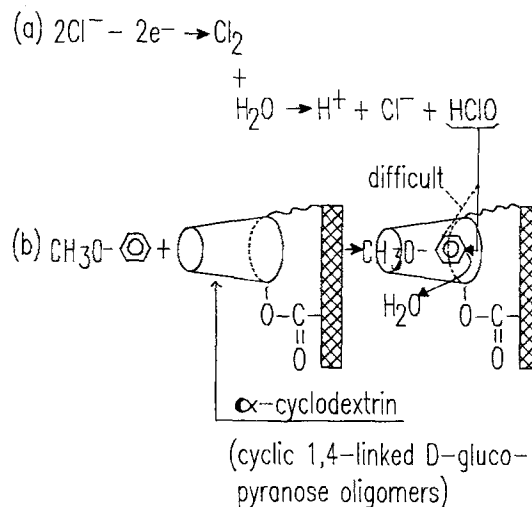
The future of applied electrochemistry is greatly dependent on the progress made in this sub-discipline. Progress and success in this domain of research can, for a large part, only be achieved through a deeper insight into what happens on the molecular level, sustained by a more quantitative approach through quantum-electrochemical calculations. Then, tailor-made electrodes can better meet the demands for higher activity (energy conservation), selectivity (conservation of raw materials, fewer by-products and thus more ecologically sound) and stability. To enhance stability built-in systems are worthy of further examination. Examples are the incorporation of clay [30], zeolites [31], ion exchanges [32], etc. In this respect, conducting ceramics, and even the superconductive materials, should be explored. In the near future, progress in the more sophisticated topics of this sub-discipline, such as the elucidation of the conduction mechanism in relation to the stereo structure and conformation of the polymer, the way chiral catalysts and enzymes should be three-dimensionally structured in a conducting matrix, the development of specific types of conducting copolymers (if possible self-doped), can lead to fascinating results.

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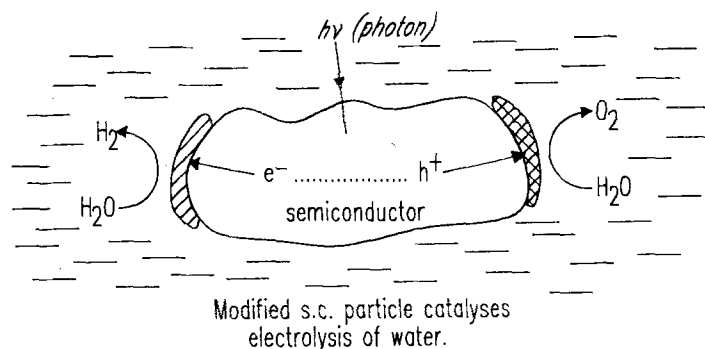

Modified s.c. particle catalyses electrolysis of water.

Fig. 15. Photo-electrolytic splitting of water with semiconducting particles, partly covered with RuO_2 and Pt.

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