Functionalized Polypyrroles. New Molecular Materials for Electrocatalysis and Related Applications

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The concept of altering the chemical structure of an electrode surface with a view to controlling the course of an electrochemical reaction was pioneered some 15 years ago by Lane and Hubbard.[1] This promising new area of electrochemistry rapidly attracted interest, the major objective being to tailor specifically the electrode material in such a way as to promote the desired electrochemical reaction.[2] The possibility of making electrodes with specific chemical, electrochemical, or optical surface properties gave rise to numerous possible applications of these "modified electrodes" in the fields of electro- and photocatalysis, electrosynthesis, electroanalysis, molecular devices, and electrochromism.

Production and applications of modified electrodes have been largely reviewed.[2,3] Electrocatalysis is a major motivation for modifying electrode surfaces,[2,3] since increasing the rate constant of electrode processes is of general interest in electrochemistry. Activation of kinetically sluggish reactions can be achieved by using appropriate electrocatalysts. Immobilizing such catalysts on an electrode surface is attractive in relation to confining and concentrating them in the vicinity of the electron source; thus the amount required to obtain an effective catalytic effect may be markedly reduced.

A rapidly developing field concerned with the creation of new catalytic electrodes involves modification by polymers. Polymer films have fundamental advantages over monolayers of catalysts covalently bonded or adsorbed.[3e,f] They show greater chemical and electrochemical stability and possess a high active-center concentration. Furthermore, they allow a greater diversity and complexity of immobilized chemical microstructures. The electrochemical polymerization and precipitation of polymer films directly on the electrode surface offers some advantages compared with their deposition as chemically preformed polymers. Electropolymerization allows the deposition of insoluble polymers, a uniform coating of irregular surfaces, and easy control of the film thickness.

Among the numerous chemical functions that could undergo electrochemical polymerization, the pyrrole group is exceptionally convenient for carrying out the

Scheme I[a]
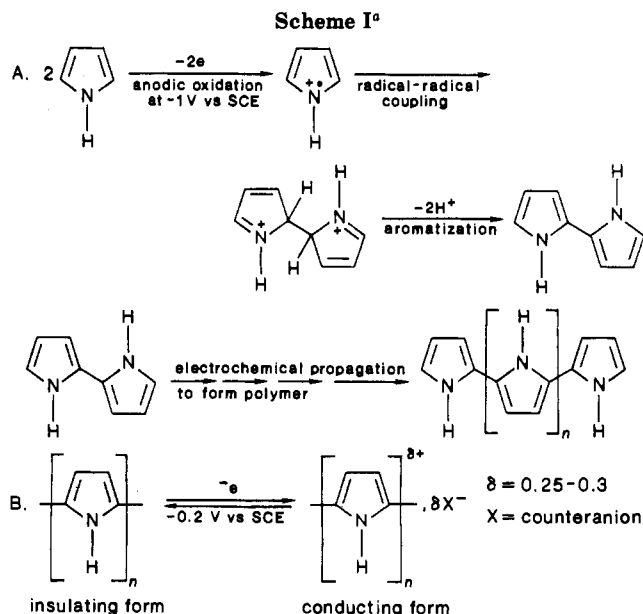
[a] (A) Mechanism for polypyrrole formation upon oxidative electropolymerization. (B) Reversible oxidation of polypyrrole.

coating of electrode surfaces by nonpassifying polymer films containing catalytic and/or redox active centers. Furthermore, polypyrrolic films are characterized by a long-term chemical stability, which allows their productive use in various applications. An account of this topic, mainly devoted to electrocatalytic applications, will be given here. A few typical extra examples, including bio- and electroanalysis, microelectronics, and electroreleasing devices, are also presented to emphasize the versatility of this type of polymeric coating.

Making Poly(pyrrole–catalyst) Modified Electrodes

Anodic electropolymerization of pyrrole occurs at a moderately positive potential[4] ($E_{1/2}$ = 1–1.3 vs SCE). The polymerization proceeds via a radical cation coupling, involving the release of two electrons and two protons per monomer.[3f,5] The resulting polymer mainly contains structural units of 2,5-linkage (Scheme I, A).

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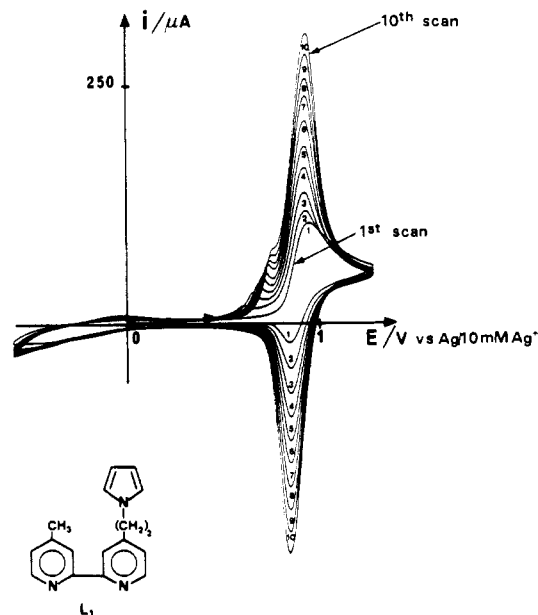
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Figure 1. Growth of a poly[pyrrole–Ru(II) complex] film during the first 10 cyclic voltammetry scans at 0.1 V s^{-1} on a 5-mm-diameter Pt disk electrode in a 0.5 mM solution of [Ru-(bpy)(L$_1$)$_2$]$^{2+}$ (bpy is the 2,2′-bipyridine) in 0.1 M nBu$_4$NClO$_4$–CH$_3$CN.

Figure 2. Cyclic voltammograms (0.1 V s^{-1}) on a 1-mm Pt disk electrode in 0.1 M nBu$_4$NClO$_4$–CH$_3$CN of (A, – – –) the pyrrole-viologen monomer V^{2+}, 0.5 mM, and of (B, —) the modified electrode obtained by the oxidation of V^{2+} at 0.85 V (4 × 10^{-5} C passed).

Polymers from pyrrole have lower oxidation potentials than the monomer. They are obtained in an oxidized, high-conductivity state with approximately one in three to four rings carrying a positive charge,[5,6] containing counterions from the electrolyte. The films can be electrochemically cycled between the oxidized, conducting state and the neutral, insulating state (Scheme I, B). Basically, there are two differents ways to functionalize polypyrrole.

Electropolymerization of Functionalized Pyrrole Monomers. Since the first report from Diaz[7] on the electrochemical coating of an electrode by a film of polypyrrole bearing redox sites, considerable effort has been made to develop electrode surface modification by the oxidative electropolymerization of pyrrole monomers, N-substituted by redox-active groups having potential catalytic activity. These include polypyridyl complexes of ruthenium(II),[8] iron(II),[8c,d] rhenium(I),[9] copper(II),[10] cobalt(II),[11] nickel(II),[12] porphyrins[13] and their cobalt,[13] nickel,[13,14] and manganese[15] metalated

complexes, a nickel(II) cyclam,[16] a copper(I) catenand,[17] ferrocene,[18] viologen (4,4′-bipyridinium salts),[19] nitroxide,[20] anthraquinone,[21] nitrobenzene[7,22] or phenothiazine[23] centers, and viologen groups covalently bound to phenothiazine, triphenylamine, or diphenylene dioxide units.[24] Moreover, the pyrrole group may be used to build more sophisticated microstructures including copolymers and multilayers containing different redox active centers,[25] which can behave as molecular electronic devices, e.g., p–n junction analogues.

From these numerous studies it appears that the pyrrole group allows the coating of a large range of surfaces, e.g., metals, oxides, or carbon electrodes, by polymeric films containing all kinds of redox, even bulky groups, and a high concentration of monomer is not required in order to grow thick films. For example, the electrooxidation of a pyrrole-containing polypyridyl complex of ruthenium(II), 0.5 mM in CH$_3$CN, allows the easy deposition of films corresponding to more than 10 000 monolayers of the ruthenium(II) complex.[8a,b] This is illustrated by Figure 1 showing the growth of a film during successive cyclic voltammetric scans, as demonstrated by the continuous increase in the size of the cyclic voltammetric peaks for the Ru$^{II/III}$ couple. On the first scan, the Ru$^{II/III}$ couple appears to be weakly reversible and the anodic peak [Ru(II) → Ru(III)] ab-

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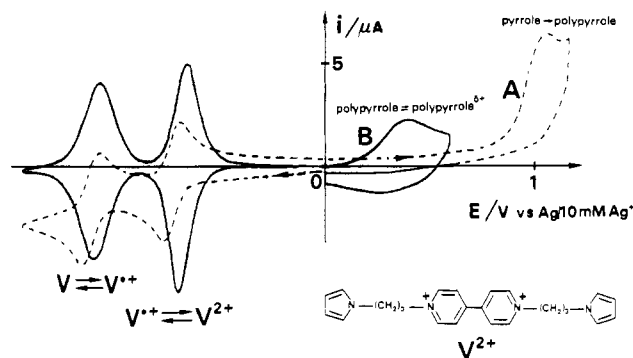
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normally high. This behavior shows that pyrrole groups are catalytically oxidized by Ru(III) species[8a,b] to give a polypyrrolic film, following the loss of two electrons and two protons per pyrrole unit.

It is noteworthy that, in spite of a dramatic drop in conductivity brought about by the N-substitution of the pyrrole unit,[26] the remaining conductivity of the poly-pyrrolic chain allows the growth of films by oxidative electropolymerization, irrespective of the electroactivity of the hanging redox group. This important point has been clearly demonstrated in the case where the redox-active center is only reducible and is illustrated in Figure 2, showing the polymerization of a pyrrole-viologen (V^{2+}) monomer.[19b] *This behavior distinguishes pyrrole polymerization from other nonpassivating electropolymerizations, like those of vinyl or amino compounds.* These require that the redox-active species bound to the polymer skeleton retain electrochemical reactivity at the potential required for the polymerization process to take place.[3e]

In contrast, direct N-functionalization of the regular polypyrrole following its deposition remains restricted to a few examples. The derivatization of polypyrrole films by ferrocene[28] or dithiocarbamate[29] moieties appeared limited to the outer surface of the film.

A new approach recently developed is to substitute pyrrole at the 3-position. In this way redox species such as ferrocene[30] and benzoquinone[31] moieties have been attached. Since substitution at the 3-position has no effect upon the electroactivity of polypyrrole, a better conductivity is expected.[30b] However, homopolymers of pyrrole–ferrocene appeared difficult to produce. Instead, copolymer films were grown from solutions containing pyrrole–ferrocene and pyrrole.[30]

Incorporation of Catalysts in Polypyrrole Films. Another route for the creation of polypyrrole-based catalytic electrodes is to incorporate catalytic sites as counteranions by the polymerization of pyrrole in a medium containing the anionic catalyst as the supporting electrolyte, or by anion exchange carried out on oxidized polypyrrole films. In this way, glutamate,[32] ferro/ferricyanide,[32,33] cobalt, iron and manganese porphyrins,[34] iron[35] and cobalt[36] phthalocyanines, and
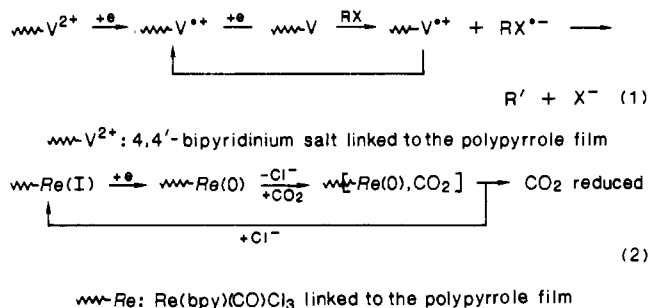
cobalt(II) salts[37] have been incorporated in polypyrrole. Such electrodes are less stable than those in which the catalyst is covalently attached to the polymeric skeleton, owing to some exchange of dopant anions with counteranions of the electrolyte. The rate of such a release is higher with small dopant anions like ferrocyanide.

Inclusion of heterogeneous catalyst microparticles has also been reported. Polypyrrole–RuO$_2$ electrodes have been prepared via incorporation of ruthenate anions by an ion-exchange procedure carried out on an oxidized polypyrrole film, followed by electroreductive precipitation of ruthenium dioxide.[38] In the same way, the inclusion of platinum particles in the film has been achieved by electropolymerization in a pyrrole solution containing suspended platinum dust[39] or via incorporation of tetrachloroplatinate anions by an ion-exchange procedure carried out on an oxidized polypyrrole film, followed by electroreductive precipitation of metallic platinum in the polymer.[40]

The range of catalysts immobilized has been extended to large biological molecules such as the enzyme glucose oxidase, which has been incorporated in polypyrrole and poly(N-methylpyrrole) by simply electropolymerizing pyrrole or N-methylpyrrole in the presence of glucose oxidase.[41] The mechanism by which the enzyme is entrapped in the polymer matrix is uncertain.

Although the electrostatic binding of catalysts within polypyrrole films appears simple and versatile, this technique has severe limitations. Polypyrrole only acts as an anion-exchange material, with an exchange capacity restricted to one negative charge per three pyrrole rings.[5,6] Furthermore, its binding capacity vanishes when it is reduced.[32,33] Ion-exchange properties of polypyrrole can be dramatically improved by linking ionic substituents to the polypyrrole backbone. The validity of this approach has been demonstrated[42] with the poly(3-methylpyrrole-4-carboxylic acid) which is able

Scheme II
Examples of Electrochemical Redox Catalysis^a and Chemical Catalysis^b on Functionalized Polypyrrole Film Electrodes

$$R' + X^- \quad (1)$$

$\wedge\wedge\wedge V^{2+}$: 4,4'-bipyridinium salt linked to the polypyrrole film

$$\text{(2)}$$

$\wedge\wedge\wedge Re$: Re(bpy)(CO)Cl$_3$ linked to the polypyrrole film

^{a} Reaction 1. ^{b} Reaction 2.

(26) A conductivity of 3 × 10^{-6} Ω^{-1} cm^{-1} has been measured[8d] for a dry poly[pyrrole–polypyridyl ruthenium(II) complex], a value that is comparable to that of poly(N-alkylpyrroles)[27] and 8 orders of magnitude lower than that of polypyrrole.

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Scheme III
A Pt/Poly[pyrrole–Ru(II) complex]–RuO₂ Electrode^a
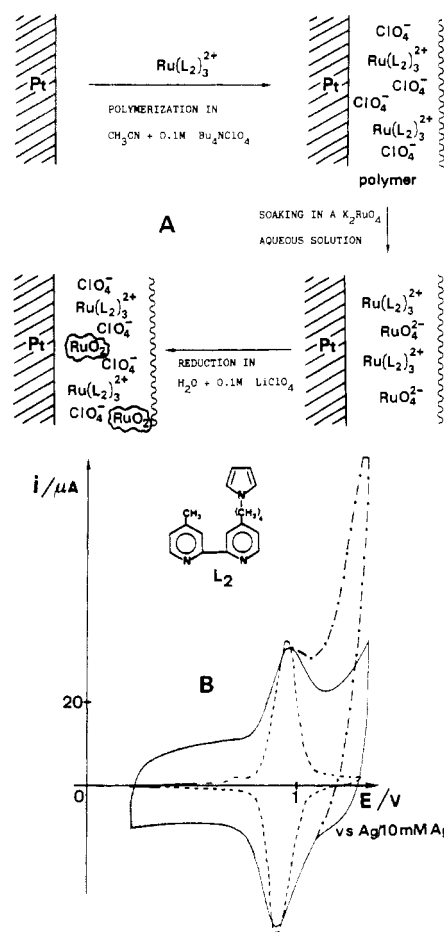
^{a} (A) Preparation procedure. (B) Cyclic voltammograms for a Pt/poly[Ru(II)] electrode [4.4 × 10⁻⁹ mol of Ru(II)] on a 5-mm-diameter Pt disk without RuO₂ (---), after incorporation of 4.3 × 10⁻⁹ mol of RuO₂ (—), and after addition of benzyl alcohol in the medium (-·-).

to bind large cations such as a bipyridinium salt or a polypyridyl complex of Co(II). Poly(pyrrole–tosylate) films[18d,43] could act in a similar way. Magnified anion-exchange properties have been obtained by using poly-*N*-alkylammoniumpyrrole. A bulky dianionic Fe–S cluster has been incorporated in such material.[44]

Finally, we have recently demonstrated[45,46] that new catalytic electrodes can be built by combining the polymerization of pyrrole monomers containing ionic redox-active groups with the inclusion by ion-exchange methods of metal or metal oxide microparticles (Scheme III). These modified electrodes display the chemical stability of the polypyrrolic film, the stable and well-defined conductivity due to redox-active groups, and the strong catalytic activity of highly dispersed metal or oxide microparticles.

Electrocatalysis Attempts

Although modified electrodes seemed at first to fail to live up to their initial promise in terms of actual

practical results, owing to their poor stability and a drop in activity following immobilization of the catalyst in a rigid medium, recent developments in the electrochemistry of polypyrrolic coatings have allowed laboratory-scale electrosynthesis to be carried out. This must be attributed to their high chemical stability, the facility of coating porous supports like carbon felt or cloth, and the association of redox species with heterogeneous catalyst microparticles in the same polymer matrix.

Cyclic[34,35,36b,37,40] and rotating disk[35,36b,37,40] voltammetric studies show that the incorporation of oxygen-reducing electrocatalysts in a regular polypyrrole matrix appears promising, as does the inclusion of platinum particles for hydrogen oxidation.[39]

On the other hand, laboratory-scale electrocatalytic synthesis on poly(pyrrole-functionalized) electrodes has been mainly carried out using organic substrates. We have recently shown that millimolar quantities of a dibromoalkane[19b,47] or a chloro ketone[48] can be dehalogenated upon reduction on platinum or carbon/poly-(pyrrole–viologen) electrodes. Despite the slow loss of catalytic activity of the electrode which occurs during the course of electrolysis, large-scale reductions have been made possible by using carbon-felt-based electrodes. This support offers a large electroactive area in a small volume and is efficiently coated by electropolymerization of N-substituted pyrroles. Although without real synthetic value, these experiments emphasize some specific features of polymer modified electrode design for electrosynthesis, which must take into account the catalytic activity of the monomer and, especially, both permeability to substrates and stability of the resulting film. Cross-linked polymers which are less active and less permeable but more stable appeared to be the best choice[19b] for the challenge of preparative-scale electrolysis. These results have demonstrated that is is possible to carry out *electrochemical redox catalysis*[49] on polypyrrole based modified electrodes. Viologen units V²⁺ included in the film act as simple electron relays, reducing the overpotential of these irreversible and kinetically slow reductions (Scheme II, reaction 1).

From a general point of view, more useful results can be obtained with polymeric films containing *chemical catalysts*,[49] which allow efficient and selective reactions. In chemical catalysis, a specific interaction and/or exchanges of atoms between the electrocatalyst and the substrate take place along with the electron transfer (Scheme II, reaction 2). The fact that many *chemical catalysts* are expensive transition-metal complexes makes advantageous the use of only a small amount of them concentrated near the electrode surface. A relevant example, which is in agreement with results obtained on a poly[vinyl–rhenium(I) complex] electrode,[50] is the electrocatalytic reduction of carbon dioxide using electrodes modified by electropolymerization of pyrrole-containing *fac*-Re(L)(CO)₃Cl complexes (L is a pyrrole-substituted 2,2′-bipyridine).[9] The large en-

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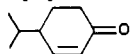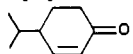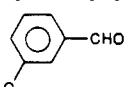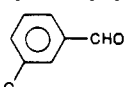(46) Cosnier, S.; Deronzier, A.; Moutet, J.-C. *Inorg. Chem.* **1988**, *27*, 2389–2390.

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<div align="center">

Table I
Electrochemical Hydrogenation on Carbon/Poly(pyrrole-viologen)-Palladium Electrodes[a]
</div>

entry	substrate	amount, mmol	consumed current, electrons/molecule	product	yield, %
1	$C_6H_5CH{=}CHCO_2H$	7	2	$C_6H_5CH_2CH_2CO_2H$	95
2	(structure)	15	2	(structure)	100
3	$C_6H_5C{\equiv}CC_6H_5$	3	4	$C_6H_5CH_2CH_2C_6H_5$	98
4	(structure) —CHO, CH_3O	4	2	(structure) —CH_2OH, CH_3O	100
5	$C_6H_5NO_2$	8	6	$C_6H_5NH_2$	86

[a] All experiments were carried out in aqueous media at pH = 1, on 20 × 20 × 10 mm carbon felt electrodes coated by polypyrrole films containing 2–5 × 10^{-5} mol of viologen units and 3–7 × 10^{-5} mol of palladium; under these conditions, currents from 100 to 300 mA were obtained when the potential was set at −0.4 to −0.5 V vs SCE.
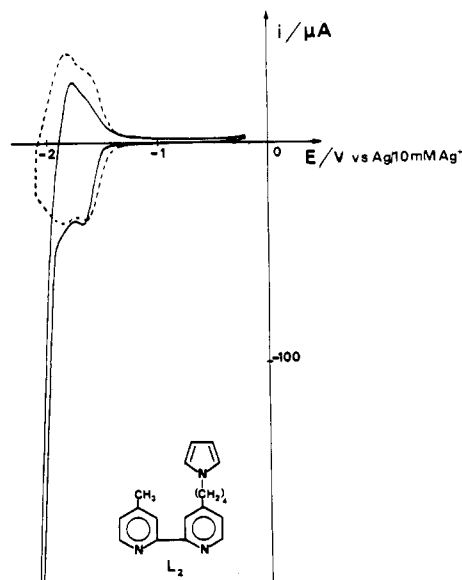

Figure 3. Cyclic voltammetry for a $Pt/poly[Re(L_2)(CO)_3Cl]$ electrode (1.7 × 10^{-9} mol of electroactive material on a 5-mm-diameter Pt disk under Ar (---) and in a CO_2-saturated solution (—); ν = 0.1 V s^{-1}.

hancement of the peak current for the reduction of the rhenium species in the presence of CO_2 is shown by Figure 3 and illustrates the strong electrocatalytic activity of this type of modified electrode toward CO_2 reduction. Preparative-scale electrolysis on platinum gauze or carbon felt modified electrodes gives mainly carbon monoxide with a current efficiency ranging from 69 to 98%, depending on the polymer used. The CO production is maximum for an optimal film thickness, corresponding to about 4000 monolayers of rhenium complex.[9b] A point that must be emphasized is the stabilization of the catalyst, which in the same experimental conditions appeared five times more stable in its polymeric form than in solution.

The electrocatalytic oxidation of carbinols on a poly(pyrrole–nitroxide) electrode[51] and the electrocatalytic epoxidation of *cis*-cyclooctadiene by molecular oxygen on a poly(pyrrole–manganese porphyrin) electrode[52] are also examples demonstrating the stabilization of an electrocatalyst through its deposition in film form on an electrode.

The only example of quantitative electrosynthesis on an anionic catalyst-doped polypyrrole modified electrode is the electroassisted oxidation of 2,6-di-*tert*-butylphenol to diphenoquinone by molecular oxygen, using a polypyrrole-containing manganese porphyrin.[34d] Results show that not only is the electrode surface involved in the process but also catalytic sites in the bulk of the polymer.

On the basis of preliminary results, catalytic electrodes built by dispersing microparticles of a heterogeneous catalyst in a redox-active polymer film appear useful in organic electrosynthesis, mainly in electrocatalytic hydrogenation. Hydrogen liberated by electrolysis in aqueous media on carbon electrodes modified by poly(pyrrole–viologen) films containing precious-metal microparticles[53] can be utilized to a large extent in reducing unsaturated organic substrates[45] (Table I). These cathodes are of high stability. For example, over 5000 molecules of cryptone (Table I, entry 2) have been hydrogenated on a poly(pyrrole–viologen)–Pd film containing 2.5 × 10^{-5} mol of Pd, while the catalytic activity of the cathode remained unchanged. The catalytic current is 2.5 times lower and 75% of catalytic activity has been lost after hydrogenation of 120 molecules of cryptone per Pd atom with a polypyrrole–Pd film containing the same amount of metal. This comparison underlines the fact that viologen groups improve markedly the conductivity and the stability of the catalytic film at −0.5 V vs SCE. This work is in progress, and new results[54] show some relevant aspects of these cathodes. At first, high catalytic activity results from the high dispersion of metal microparticles in the polymeric matrix. This is clearly demonstrated by the hydrogenation of styrene on a carbon/poly(pyrrole–viologen)–Pt electrode which affords ethylbenzene with a 56% electric yield, while the same reduction on a conventional platinized platinum electrode was unsuccessful.[55] Another important point is the strong improvement of the catalytic efficiency obtained with a small increase in metal loading of the film, in the case of a "hard-to-hydrogenate" substrate like isophorone.[54] Moreover, as in catalytic hydrogenation, reduction of polyunsaturated molecules can be directed by choosing the catalytic metal to be incorporated in the film.[56] In

(51) Deronzier, A.; Limosin, D.; Moutet, J.-C. *Electrochim. Acta* **1987**, *32*, 1643–1647.

(52) Moisy, P.; Bedioui, F.; Robin, Y.; Devynck, J. *J. Electroanal. Chem.* **1988**, *250*, 191–199.

(53) Pt, Pd, or Rh is incorporated by following a similar procedure to that shown in Scheme III. Metal salts MX_y^{n-} are incorporated as counteranions in the polymer and then reduced to their metal form.

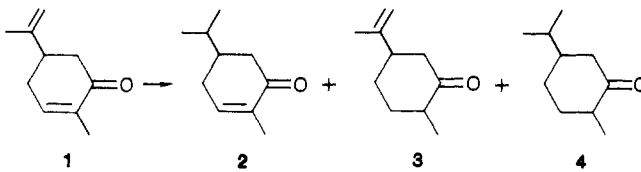(54) Coche, L.; Limosin, D.; Moutet, J.-C., to be published.

(55) Casadei, M. A.; Pletcher, D. *Electrochim. Acta* **1988**, *33*, 117–120.

(56) Coche, L. Thesis, Université Joseph Fourier Grenoble I, France, 1987.

Table II
Hydrogenation of Carvone*[a]*

metal (amount)	consumed current, electrons/ molecule	relative percentages				total current efficiency, %
		1	2	3	4	
Pd	2	35	8	37	20	85
(70 μmol)	4	22	1	17	60	70
Rh	2	36	36	2	26	90
(45 μmol)	4	4	30	1	63	80

[a] Experimental conditions as in Table I.

the case of carvone (Table II), the ability of Pd to reduce preferably the carbon–carbon double bond in the cycle compares well with the easy hydrogenation of the vinylic bond using a Rh-containing cathode.

Similar modified electrodes have been designed for the oxidation of organic substrates.[46] RuO_2 particles were incorporated in poly[pyrrole–trisbipyridyl Ru(II) complex] films (Scheme III). As a matter of fact, the potential of the $Ru^{II/III}$ reversible redox system lies around 1 V vs Ag/10 mM Ag^+, ensuring a large conductivity in the region where strong oxidizing agents[57] like RuO_4 or RuO_2 could be produced.[58] Analytical results have clearly shown that RuO_4^{2-}, RuO_4^-, and RuO_4 species can be formed in the polymer film, starting with a poly[pyrrole–Ru(II) complex]–RuO_2 electrode and scanning the potential up to 1.8 V. The potentials of these transformations in these unusual conditions have been specified.[46] Finally, preparative-scale electrolysis at 1.16 V allowed the selective transformation of millimolar quantities of benzyl alcohol to benzaldehyde with a turnover (moles of benzaldehyde formed to moles of RuO_2 in the film) close to 5000. The comparatively weak catalytic activity and stability of a poly(pyrrole–viologen–RuO_2) electrode[59] demonstrates the role of the polypyridyl Ru(II) complex as a useful electron relay, which improves the stability and conductivity of the film at the high oxidation potentials required to produce oxidizing RuO_2 derivatives.

Other Areas of Applications

In addition to their potential use of synthetic electrocatalytic processes, functionalized polypyrrole films have attracted interest in various fields such as biosensors, electroanalysis, macromolecular electronics, or electroreleasing devices.

As already mentioned, the enzyme glucose oxidase can be immobilized in polypyrrole and poly(N-methylpyrrole).[41] Such a procedure provides a simple and easily controlled enzyme immobilization that has application in the development of glucose sensors.

(57) Mijs, W. J.; De Jonge, C. R. H. I. *Organic Synthesis by oxydation with Metal Compounds*; Plenum Press: New York and London, 1986; pp 445–467.
(58) Successive reversible transformations $RuO_4^{2-} \rightleftharpoons RuO_4^- \rightleftharpoons RuO_4$ are known to be 1.35–1.45 V and 1.68–1.80 V vs NHE, respectively, in aqueous solution. Burke, L. D.; Whelan, D. P. *J. Electroanal. Chem.* 1979, *103*, 179–187.
(59) Here, cationic viologen groups allowed incorporation of RuO_2 by the anion-exchange procedure.[46] The conductivity of the film in the anodic region can only be due to the polypyrrolic chain.
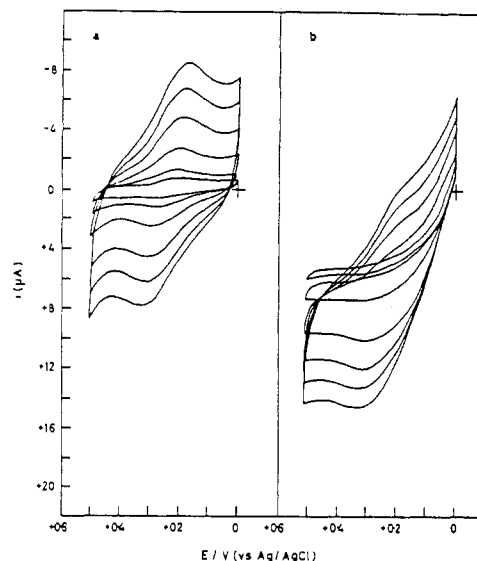

Figure 4. Electrochemical response of a poly(pyrrole–ferrocene)–glucose oxidase film in phosphate buffer (pH 5.6) at different sweep rates (5, 10, 25, 50, 75, and 100 mV s^{-1}) in the absence (a) and in the presence (b) of glucose; from ref 30c.

However, the electrical communication between the active center of the enzyme and the electrode material requires the presence of mediators like oxygen, ferrocene, or other electron acceptors. Simultaneous immobilization of glucose oxidase and ferrocenecarboxylate provides a biosensor capable of detecting glucose without use of any mediator in solution.[41d] Use of a polypyrrole film N-substituted by ferrocene groups offers an attractive way to realize in one simple electrodeposition step a reagentless sensor (Figure 4) in which problems associated with leaching mediators are circumvented.[30c]

Funtionalized polypyrrole also offers possibilities in electroanalysis. For example, polypyrrole films covalently N-substituted by carbodithioate groups have been used for the determination of metal ions in solutions,[29] with a detection limit of 1 ppm.

New developments can be considered from first results on functionalized polypyrrole-based microelectronic devices, taking into account the chemical specificity of redox systems linked to the polypyrrole backbone. A pH-sensitive microelectrochemical transistor illustrated such a capability.[19c] The principle of this device is based on the pH dependence of the reduction potential of a poly(pyrrole–VH^{2+}) material, in which VH^{2+} is a protonated monoquaternized 4,4'-bipyridinium group. At fixed gate voltage, the source-drain current is pH dependent, as a result of the reversible protonation of the bipyridinium group.

Reversible ion-exchange properties of the regular polypyrrole have been used to design electroreleasing systems. The basic concept is to bind a reagent, e.g., a drug, into a polymer film deposited on an electrode, to release this reagent at a constant rate, and to spatially target by applying an electrochemical pulse.[60] A simple approach is the incorporation of an anionic reagent as counterion in an oxidized polypyrrole film. Reduction releases the reagent in solution, following the neutralization of the polymer. This approach has been

(60) Lau, A. N. K.; Miller, L. L. *J. Am. Chem. Soc.* 1983, *105*, 5271–5277.

successfully demonstrated[32] in the case of polypyrrole doped with glutamate anions, a drug of interest for neuroscience.

Conclusion

Among the numerous procedures for electrode-surface modification by polymer films, the building of microstructures based on the electropolymerization of pyrrole and substituted pyrroles appears to be a versatile way of designing promising electrode materials. Easy to be formed, leading to remarkably stable coating, allowing the anchorage of complex and/or bulky molecules and the building of structures where spatially separated catalysts act together, functionalized polypyrroles are good candidates for the development of electrocatalysis on modified electrodes. Although their electronic conductivity brings a matchless advantage for their preparation and their application in a restricted anodic area, it is noteworthy that polypyrrole films can be effectively used at cathodic or high anodic potentials when suitable redox relays are attached to the polypyrrole skeleton or included in the polymeric matrix.

Apart from promising results in electrocatalysis with an aim of synthetic applications, the few examples stated above show the large and versatile possibilities offered by these new molecular materials. It is still expected that new areas of important applications can be developed for polymer-modified electrodes. Functionalized polypyrroles are among the best candidates and will certainly help to put into concrete form the great promise associated with the concept of manipulating chemical and electrochemical properties of electrode surfaces.