

Polypyrrole films containing rhodium(I) and iridium(I) complexes: improvement in their synthesis and electrocatalytic activity in aqueous media

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Abstract

Functionalized polypyrrole films containing $M^I(L)(diene)]^+$ complexes (M = rhodium or iridium, L = substituted 2,2'-bipyridine or 1,10-phenanthroline) have been synthesized by complexation of $[M^I(diene)CL]_2$ precursor complexes in polyL films pre-coated on carbon and platinum surfaces by oxidative electropolymerization of pyrrole-substituted polypyridyl ligands, and characterized by cyclic voltammetry and X-ray photoelectron spectroscopy. The efficiency of the in situ complexation reaction appears strongly dependent on the permeability of the ligand film. The electrochemical behaviour in aqueous electrolyte and the electrocatalytic activity of these metallopolymers towards water reduction and hydrogenation of unsaturated organic substrates is described.

Keywords: Modified electrodes; Electrocatalysis; Metallopolymer films; Rhodium and iridium complexes; XPS

1. Introduction

The modification of electrode surfaces by polymer films containing molecular catalysts affords a means to design molecular electrodes exhibiting the catalytic activity of the immobilized reagent [1]. In that context, the immobilization of transition metal complexes in poly(pyrrole) films coated on electrode surfaces has shown its potential interest for applications in electrocatalysis [2]. Attractive applications of these molecular electrode materials are reduction of protons or water to dihydrogen, and electrocatalytic hydrogenation (ECH) which is the reaction of unsaturated organic substrates with hydrogen formed onto the catalytic electrode [3]. It has been demonstrated in our laboratory that the coating on carbon electrodes of polymer films by oxidative electropolymerization of $[Rh^{III}(C_5Me_5)(L)Cl]^+$ [4,5], $[Rh^{III}(L)_2(Cl)_2]^+$ [6,7], $[Rh^{III}(L)(P)_2(Cl)_2]^+$ [8] and $[Pd^{II}(L)_2]^{2+}$ [9] complexes (L is a pyrrole-substituted

2,2'-bipyridine or 1,10-phenanthroline, P is PPh_3 Et or PPh_4) allows us to synthesize active polymeric electrode materials for hydrogen evolution [4–6] and ECH of carbon–carbon and carbon–oxygen double bonds [6–10] in aqueous electrolytes. It is assumed that reduction of protons or water by the metal complex in a low valence state leads to a metal–hydride intermediate from which hydrogen gas is evolved, or a substrate hydrogenated.

In the pursuit of our interest in the preparation of new polypyrrole-based electrode materials, we have recently reported [11] the synthesis of poly(pyrrole- $[M^I(L)(diene)]^+$) film modified electrodes (M = rhodium or iridium, diene = COD or NBD, namely 1,5-cyclooctadiene or 2,5-norbornadiene), by complexation of $[M^I(diene)CL]_2$ precursor complexes in polyL films coated on electrode surfaces by oxidative electropolymerization of pyrrole-substituted polypyridyl ligands. These modified electrodes were characterized from cyclic voltammetry experiments in organic electrolytes. In the present paper, we first demonstrate that their elaboration procedure can be improved by increasing

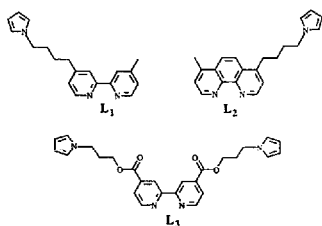
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the permeability of the ligand films. In addition, further characterization of the films by X-ray photoelectron spectroscopy has been performed. We also describe the electrochemical behaviour and the electrocatalytic activity in aqueous media of these modified electrodes. Furthermore, since N-heterocyclic complexes of rhodium(I) and iridium(I) containing π -bonding ligands are known as active catalysts for the hydrogenation of olefins and ketones [12,13], we have evaluated the behaviour of these metallopolymer films towards the ECH of organic substrates.

2. Results and discussion

2.1. Synthesis and characterization of $\text{poly}[\text{M}^{\text{I}}(\text{L})(\text{diene})]^+$ film electrodes

Very recently, we have shown that $[\text{M}^{\text{I}}(\text{diene})\text{Cl}]_2$ precursor complexes ($\text{M} = \text{Rh}$ or Ir , diene = COD or NBD) readily react with polymer films coated on carbon and platinum surfaces by oxidative electropolymerization of pyrrole-substituted 2,2'-bipyridine and 1,10-phenanthroline ligands L_1 , L_2 and L_3 [11]. The resulting $\text{poly}[\text{pyrrole}-\{\text{M}^{\text{I}}(\text{L})(\text{diene})\}]^+$ metallopolymer films were characterized from cyclic voltammetry experiments in acetonitrile (MeCN) electrolyte. PolyL films were usually synthesized in acidic (10^{-1} M HClO_4) MeCN containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). As a matter of fact, the oxidative electropolymerization of pyrrole-polypyridyl compounds is inefficient in neutral electrolytes. In contrast, clean polymerization takes place when the N atoms of the pyridyl moieties of the monomers are complexed with protons [11,14,15]. We find that the complexation process in pre-formed polyL films became slower and slower as the film thickness increased, and was totally inefficient in films of large size, i.e. with apparent surface coverages of ligand Γ_L higher than 5×10^{-8} mol cm^{-2} . This was attributed to the poor permeability of the thick polymer films [11].



For electrocatalytic application of these new molecular electrode materials, it is of obvious importance to synthesize films with higher permeability and containing larger amounts of catalytic sites. A way to improve the degree of order and the permeation through polypyrrole [16,17] and functionalized polypyrroles [18] is to carry out the polymerization step in an electrolyte containing a bulky anion such as an arylsulfonate instead of the smaller perchlorate anion, which might produce films with expanded structures. It is anticipated that the counter anion imposes a minimum pore/cavity size corresponding to its volume [19]. It should be emphasized that in the course of the electropolymerization of pyrrole-substituted polypyridyl ligands in acidic electrolyte, besides anions entrapped as dopants of the polypyrrole matrix two counter anions per monomeric unit are also incorporated in the film, since the protonated ligand carries a double positive charge. Subsequent exchange of incorporated arylsulfonate anions with smaller ones such as perchlorate or tetrafluoroborate anions should leave large pores in the polymer [20], which are able to ensure better mass transport of reactants through the film.

Attempts at the electropolymerization by controlled-potential oxidation at 0.85 V of 10^{-2} M monomer L_1 in MeCN containing 0.1 M tetraethylammonium *p*-toluenesulfonate (TEAS) and 0.15 M *p*-toluenesulfonic acid were unsuccessful. Obviously, this electrolyte is not acidic enough to ensure the protonation of the pyridyl moieties of the monomer. In contrast, clean electropolymerization takes place by using a mixture of TEAS (0.1 M) and HClO_4 (0.15 M) as supporting electrolyte. Formation of a conducting polypyrrolic film onto the electrode surface is evidenced (Fig. 1(A)) by the quasi-reversible redox peak system centred around 0.3 V exhibited by the modified electrode transferred and cycled in fresh MeCN-tetramethylammonium tetrafluoroborate (TMAF). Γ_L can be roughly estimated from the charge under the polypyrrole oxidation wave, assuming that one-in-three pyrrole units is oxidized [21]. Poly L_1 films prepared in this way were then tested towards the *in situ* complexation of the $[\text{Rh}(\text{COD})\text{Cl}]_2$ precursor complex in DMSO-TMAF electrolyte, to form $\text{poly}[\text{Rh}(\text{L}_1)(\text{COD})]^+$ films. We first noticed that complexation of all binding sites is very fast in poly L_1 films of $\Gamma_L \approx 5 \times 10^{-8}$ mol cm^{-2} . In these experimental conditions, the height of the reversible peak system corresponding to the $[\text{Rh}(\text{L}_1)(\text{COD})]^{+/0}$ redox couple in the film ($E_{1/2} = -1.52$ V [11]) rose quickly to reach its maximum value after a few scans. Determination of the loading of the complex from the charge under the reduction wave showed that the incorporation ratio (defined as the ratio of the amount of immobilized complex/amount of bpy units in the film) was close to 100%. This contrasts with the quite inefficient complexation of Rh(I) species in poly L_1 films of similar size

and prepared in TBAP–MeCN electrolyte [11]. Furthermore, the reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ was very slow, but effective in poly L_1 films of larger size (around $10^{-7} \text{ mol cm}^{-2}$). This is demonstrated in Fig. 1, which shows in the negative potential area the steady increase of the $[\text{Rh}(\text{L}_1\text{XCOD})]^+ / [\text{Rh}(\text{L}_1^-\text{XCOD})]^0$ peak system in a thick poly L_1 film upon repeated scans in DMSO electrolyte containing $10^{-3} \text{ M } [\text{Rh}(\text{COD})\text{Cl}]_2$, to reach a stable voltammogram after 200 cycles (Fig. 1(B)). The cyclic voltammetry curve for the $\text{C}/\text{poly}[\text{Rh}(\text{L}_1\text{XCOD})]^+$ modified electrode prepared in this way and transferred to fresh MeCN–TMAF electrolyte shows a stable, well-behaved reduction wave (Fig. 1(C)) from which can be calculated an apparent surface concentration of rhodium species Γ_{Rh} of $8.6 \times 10^{-8} \text{ mol cm}^{-2}$. Evidently, the electropolymerization of L_1 in a medium containing a mixture of *p*-toluenesulfonate (from TEAS) and perchlorate (from HClO_4) counter anions in a 2/3 ratio, instead of the sole perchlorate anion, allows us to synthesize more permeable free ligand films from which can be elaborated thicker metalopolymer films.

The effective building of $[\text{Rh}(\text{LXCOD})]^+$ moieties in poly L_1 films was also established from X-ray photoelectron spectroscopy (XPS) experiments carried out with films coated on Pt electrodes. Emission of electrons with different binding energies (BE) due to the presence of various elements including O 1S (531 eV), N 1S

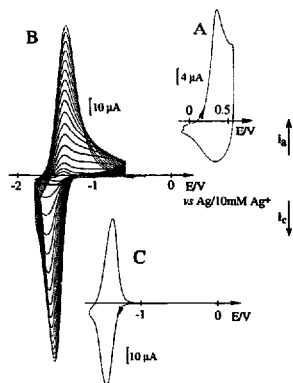


Fig. 1. (A) Cyclic voltammogram in 0.1 M TMAF–MeCN of a poly L_1 film coated on a carbon disc electrode (diameter 3 mm) by oxidative electropolymerization at 0.85 V (charge passed 2.1 mC) in MeCN containing 0.01 M L_1 , 0.1 M TEAS and 0.15 M HClO_4 ; scan rate 0.05 V s^{-1} . (B) The same electrode cycled in 0.1 M TMAF–DMSO containing 1 mM $[\text{Rh}(\text{COD})\text{Cl}]_2$ (every 10th scan recorded); scan rate 0.05 V s^{-1} . (C) The $\text{C}/\text{poly}[\text{Rh}(\text{L}_1\text{XCOD})]^+$ modified electrode synthesized as described above ($\Gamma_{\text{Rh}} = 8.6 \times 10^{-8} \text{ mol cm}^{-2}$), transferred to pure TMAF–MeCN electrolyte, scan rate 0.02 V s^{-1} .

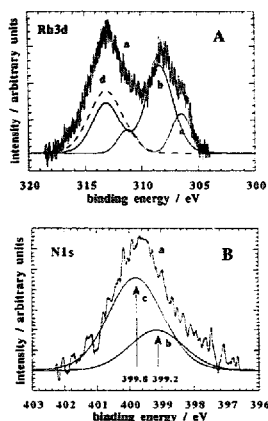


Fig. 2. Experimental (curves a) and deconvoluted (curves b, c, d) XPS spectra for a $\text{poly}[\text{Rh}(\text{L}_1\text{XCOD})]^+$ film coated on Pt. (A) The Rh 3d region: the spectrum a is fitted with two doublets (b, c) attributed to Rh^I and Rh^0 respectively, and a single peak (d) attributed to Pt. (B) The N 1s region: the spectrum a is fitted with two peaks (b, c) attributed to free and complexed aromatic N atoms respectively.

(399 eV) and C 1S (284.5 eV) was observed with a pure poly L_1 film. An additional peak at 314 eV was attributed to the Pt support ($\text{Pt } 4d_{5/2}$). Rh^I was clearly present in poly L_1 films which have been cycled in DMSO electrolyte containing $[\text{Rh}(\text{COD})\text{Cl}]_2$ to build up $[\text{Rh}(\text{L}_1\text{XCOD})]^+$ moieties in the polymer bulk. For example, Fig. 2(A) presents the binding energy region for the Rh 3d core level peaks (304–318 eV) for a $\text{poly}[\text{Rh}(\text{L}_1\text{XCOD})][\text{ClO}_4]$ film. From deconvolution of the experimental curve a (see Section 4), two main peaks are seen at 308.41 eV ($3d_{5/2}$) and 313.16 eV ($3d_{3/2}$) (Fig. 2(A), curve b). These peak values compare well with those (308.30 and 312.95 eV) for the $[\text{Rh}(\text{dmbpy})(\text{COD})][\text{BF}_4]$ model complex (dmbpy = 4,4'-dimethyl-2,2'-bipyridine), which was coated on a Pt sheet by evaporation of a droplet of solution in MeCN. Furthermore, the BE ($3d_{5/2}$) for Rh at 308.41 eV agrees with XPS data (307.5 to 308.7 eV) reported in the literature for various Rh^I complexes [22]. It should be noted that the pair of small peaks (306.45 and 312.20 eV, Fig. 2(A), curve c) which appear in the experimental curve as shoulders on the main Rh^I peaks can be attributed to the presence of some metallic rhodium (307.0 and 311.75 eV in the literature [22]). Obviously, some decomposition of Rh^I complexes to Rh^0 occurred upon the reductive cyclic voltammetry scans which were performed to characterize this

poly[Rh(L)₁(COD)]⁺ film. An additional peak (316 eV, curve d) can be attributed to the Pt support. Furthermore, in the spectrum recorded for a pure polyL₁ film, the N 1S peak appears at a high BE (399.26 eV) characteristic of aromatic nitrogen atoms [23]. This peak corresponds to the N atoms of both the pyrrolic and the pyridyl rings. After complexation with Rh^I, this peak has broadened and is shifted to higher energies (Fig. 2(B)). From deconvolution of the spectrum, two peaks are seen at 399.16 and 399.80 eV, with a 1/2 surface ratio (Fig. 2(B)). The first one (curve b) is located at the same energy as in pure polyL₁, and therefore can be attributed to the N atoms of the pyrrolic groups. The peak which appears at a higher energy (curve c) can be reasonably ascribed to the N atoms of the complexed bipyridyl groups. Its BE compares with the BE (399.90 eV) for the N atoms in the [Rh(dmbpy)(COD)](BF₄) model complex. The 1/2 surface ratio found for these two N 1S peaks indicates that all the pyridyl sites in the polyL₁ film are complexed with Rh^I.

Studies on the activity of [M(L)(diene)]⁺ complexes (L = 2,2'-bipyridine or 1,10-phenanthroline) as hydrogenation catalysts have shown that [M(L)(ED)]⁺ derivatives (ED = 1,5-hexadiene) are more reactive in comparison with the complexes with other diolefins, i.e. COD or NBD [12,13,24]. This was attributed to the higher lability and lower stability of the π -olefinic bond, due to the flexibility of the 1,5-hexadiene ligand [13]. In addition it is known that ED complexes decompose in MeCN, yielding very complicated cyclic voltammetry curves [25]. We tried to synthesize poly[Rh(L)(ED)]⁺ films (L = L₂ or L₃), since some stabilization of the ED complex might be expected following their entrapment in a polymeric matrix. The cyclic voltammetry curve in MeCN electrolyte for a carbon modified electrode obtained by treating in DMSO a polyL₁ film with [Rh(ED)Cl]₂ is shown in Fig. 3 (curve a). Obviously, the shape of the voltammogram is markedly different from that for a poly[Rh(L₁(COD))] film for example (Fig. 3, curve b). Since the reduction potentials of [Rh(L)(diene)]⁺ complexes are known to

be quite insensitive to changes of diene [11,25,26], it is anticipated that the reaction of [Rh(ED)Cl]₂ into polyL₁ does not yield to the formation of stable [Rh(L)(ED)]⁺ moieties in the polymer phase. The cyclic voltammetry curve clearly shows two reversible waves ($E_{1/2} = -1.77$ and -2.06 V) with a sharp pre-peak ($E_{pc} = -1.71$ V) at the negative foot of the first reduction wave. These electrochemical features are similar to those already observed with poly[Rh^{III}(L₁)₂(Cl)₂]⁺ film modified electrodes [6,27]. Furthermore, the half-wave potentials of the surface couples are in close correspondence with those for the model complex [Rh(dmbpy)₂(Cl)₂]⁺ ($E_{1/2} = -1.79$ and -2.03 V for the two-ligand-based reversible one-electron reduction [27]). These observations strongly suggest that the rhodium species in the polymer film are mainly of the type [Rh^I(L)₂]⁺. They are probably formed following the release of ED from the precursor complex and the complexation of some metal centres with two bpy units of the film. In agreement with this suggestion, it has been shown [13] that [Rh(L)(ED)]⁺ complexes (L = 2,2'-bipyridine or 1,10-phenanthroline) lose the diolefin in MeCN solution to give [Rh^I(L)₂]⁺ complexes in the presence of an excess of L.

2.2. Electrochemical behaviour of poly[M^I(L)(diene)]⁺ films in aqueous electrolytes

Immobilization of these metal complexes in a film form onto an electrode surface offers the opportunity to study their electrochemical behaviour in aqueous media. In basic aqueous electrolytes (equimolar phosphate buffer + ethanol mixture, pH 9), the [Rh^I(L₁(COD)]⁺/[Rh^I(L₁)(COD)]⁰ redox peak system in the film becomes irreversible (Fig. 4(A), curve a), and catalytic currents were observed by potentiostating glassy carbon disc modified electrodes at -1.4 V vs. SCE. In the same experimental conditions, very low currents were obtained on bare glassy carbon (Fig. 4(A), curve b). As previously shown with other polypyridyl rhodium complex-based materials [5,8], these observations indicate the electrocatalytic behaviour of the immobilized [Rh(L₁(COD))] complex towards water reduction and hydrogen evolution. We have then checked the operational stability of these molecular electrode materials. With the modified electrode described in Fig. 4 (diameter 5 mm, $\Gamma_{Rh} = 1.1 \times 10^{-8}$ mol cm⁻²), the initial current density (0.14 mA cm⁻² at -1.4 V) dropped to 0.04 mA cm⁻² after the consumption of 0.2 C. This corresponds to a turnover (ratio of mole of protons reduced to mole of immobilized Rh species) of 960. The loss of catalytic activity of the modified electrode can be attributed to a slow degradation of the metallopolymer during the electrolysis. This assumption has been corroborated by the study of the electrochemical response of the modified electrode in MeCN elec-

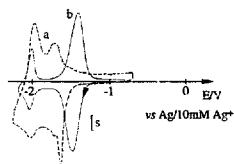


Fig. 3. Cyclic voltammograms in 0.1M TBAP-MeCN, scan rate 0.05 V s⁻¹: curve a: C/polyL₁ modified electrode (diameter 5 mm, $\Gamma_{Rh} = 2.1 \times 10^{-8}$ mol cm⁻²) which has been reacted in DMSO with [Rh(ED)Cl]₂, $i_s = 4$ μ A; curve b: C/poly[Rh(L₁(COD))] modified electrode (diameter 5 mm, $\Gamma_{Rh} = 10^{-8}$ mol cm⁻², $i_s = 10$ μ A).

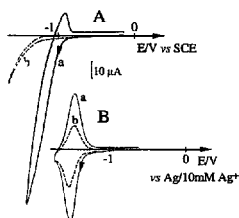


Fig. 4. (A) Curve a: cyclic voltammogram of a $C/poly[Rh(L_1)(COD)]^+$ modified electrode (diameter 5 mm, $\Gamma_{Rh} = 1.1 \times 10^{-8} \text{ mol cm}^{-2}$) in an equimolar phosphate buffer (pH 9) + EtOH mixture: curve b: electrochemical response of a bare carbon electrode in the same experimental conditions. (B) Cyclic voltammetry curves in TBAP-MeCN of the same modified electrode before (curve a) and after (curve b) controlled potential electrolysis at -1.4 V (charge passed 0.2 mC) in phosphate buffer, scan rate 0.05 V s^{-1} .

trolyte before (Fig. 4(B), curve a) and after (Fig. 4(B), curve b) electrolysis in aqueous electrolyte. The drop in electroactivity corresponds to a loss of 53% of complex, as estimated from the decrease of the integrated current under the first ligand-based reduction wave.

While $C/poly[Rh(L_2)(COD)]^+$ modified electrodes display the same behaviour as the corresponding L_1 -based electrode materials, $poly[Rh(L_3)(COD)]^+$ and $poly[Ir(L_1)(COD)]^+$ films are quickly transformed upon cycling in aqueous electrolytes. After transfer to fresh MeCN electrolyte, their cyclic voltammograms present new redox peak systems. In the case of $C/poly[Rh(L_3)(COD)]^+$ electrodes, the electrochemical features of the transformed film indicate that $[Rh(L_3)_2]^+$ species are formed in the film. As a matter of fact, the

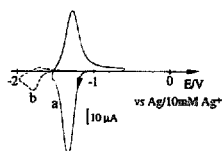


Fig. 5. Cyclic voltammograms of a $C/poly[Ir(L_1)(COD)]^+$ modified electrode (diameter 5 mm, $\Gamma_{Ir} = 1.1 \times 10^{-8} \text{ mol cm}^{-2}$) in TBAP-MeCN electrolyte, before (curve a) and after (curve b) a few reductive scans in phosphate buffer (pH 4.2), scan rate 0.05 V s^{-1} .

regular ligand-based reduction wave ($[Rh(L_3)(COD)]^+/[Rh(L_3)(COD)]^0$, $E_{1/2} = -1.04 \text{ V}$ [11]) is replaced by a weak reversible peak system ($E_{1/2} = -1.53 \text{ V}$) which closely corresponds to that reported for the first ligand-based reduction for the immobilized $[Rh^{III}(L_3)_2(CI)_2]^+$ complex ($[Rh^I(L_3)_2]^+/[Rh(L_3)(L_3)]^0$, $E_{1/2} = -1.45 \text{ V}$ [27]). On the other hand, transformed $poly[Ir(L_1)(COD)]^+$ films (Fig. 5) only show a new quasi-reversible redox couple ($E_{1/2} = -1.78 \text{ V}$ instead of -1.29 V [11]) which cannot be clearly attributed at the present time.

2.3. Electrocatalytic hydrogen generation and hydrogenation of unsaturated substrates on $poly[Rh(L)(COD)]^+$ films ($L = L_1, L_2$) in aqueous electrolytes

To corroborate the catalytic activity of the immobilized complex toward H_2O electroreduction, we have performed a preparative-scale electrolysis in the same experimental conditions as above, on a carbon felt electrode ($10 \times 10 \times 4 \text{ mm}^3$) coated with a film contain-

Table 1
Electrocatalytic hydrogenation of 2-cyclohexen-1-one, carvone, and acetophenone on $C/poly[Rh(L)(COD)]^+$ ($L = L_1, L_2$) modified electrodes^a

Entry	Ligand	Amount of immobilized complex (μmol)	Substrate ^b	Product	Consumed current (electrons per molecule)	Yield (%)	Current efficiency (%)	Turnover ^c [turnover per hour]
1	L_1	0.64			2	40	40	625 [93]
2	L_1	0.96			0.9	25	56	260 [34]
3	L_2	0.51			0.25	7	61	137 [21]
4	L_1	0.95			0.9	12	27	
5					3.2	31 ^f	19	326 [21]
6	L_1	0.95			2	4	4	42 [5]

^a Carried out on carbon felt modified electrodes in 25 ml of an equimolar phosphate buffer + ethanol mixture (pH 7) at -1.4 V vs. SCE.

^b 1 mmol.

^c Yields determined by GC.

^d Two times the ratio mole of product to mole of electrons passed, taking into account that the HEC of a carbon-carbon double bond consumes 2 electrons per molecule.

^e The ratio mole of product to mole of immobilized catalyst.

^f The reaction mixture contained traces of dihydrocarveol.

ing 1.4×10^{-6} mol of $[\text{Rh}(\text{L})_3(\text{COD})]^+$ species. The electrolysis current (approximately 10 mA) was fairly stable, and 0.2 C was passed after 2 h 37 min of electrolysis. H_2 was produced with a quantitative current efficiency corresponding to a turnover of 720 (turnover per hour 274). Under the same experimental conditions the current was less than 1 mA on a bare carbon felt electrode, and only a few coulombs could be passed.

It is known that $[\text{Rh}(\text{bpy})\text{S}_2]^+$ species (S = solvent) which form in alkaline methanol solution under reductive conditions from $[\text{Rh}(\text{bpy})(\text{diene})]^+$ complexes are good hydrogenation catalysts for activated carbon-carbon double bonds, as those in α,β -unsaturated esters and ketones [24]. In this context, we have checked the electrocatalytic activity of $[\text{poly}(\text{Rh}(\text{L})_3(\text{COD}))]^+$ ($\text{L} = \text{L}_1, \text{L}_2$) film modified electrodes towards the ECH of unsaturated organic substrates. Results from preliminary experiments carried out with 2-cyclohexen-1-one (Table 1, entries 1, 2, 3) and carvone, namely the (R)-5-isopropenyl-2-methyl-2-cyclohexenone (Table 1, entries 4, 5) show that the corresponding cyclohexanone and dihydrocarvone were produced in moderate yield, and with satisfactory current efficiencies and turnovers. We also found that the reduction of acetophenone was poorly efficient (Table 1, entry 6). It should be noted that saturated ketones are not reduced on these catalytic cathodes. Only traces of dihydrocarvone could be detected when the hydrogenation of carvone was carried on up to the consumption of 3.2 electrons per molecule of substrate (Table 1, entry 5). This selectivity clearly shows that the catalytically active species in the polymer films are truly of the type $[\text{Rh}(\text{L})(\text{COD})]^+$ or $[\text{Rh}(\text{L})\text{S}_2]^+$, and not $[\text{Rh}(\text{L})_2]^+$. As a matter of fact, we have already demonstrated that carbon electrodes modified by electropolymerization of $[\text{Rh}(\text{L})_2(\text{Cl})_2]^+$ complexes ($\text{L} = \text{L}_1, \text{L}_2, \text{L}_3$) are efficient cathodes for the ECH of cyclohexanone, 2-cyclohexen-1-one and their substituted derivatives, to their corresponding cyclohexanols [6,7,10]. It could also be anticipated that electroreductive degradation of Rh^I species leads to metallic rhodium as small clusters, which would form catalytic centres in the film. However, in this case the hydrogenation of carvone would give preferably carvotanacetone instead of dihydrocarvone, as previously observed in the course of its reduction on polymer films containing dispersed Rh^0 microparticles [28].

All the ECH experiments described above were performed on carbon felt electrodes coated with $[\text{poly}(\text{Rh}(\text{L})_3(\text{COD}))]^+$ films, elaborated from polyL_1 films synthesized in TBAP-MeCN electrolyte. An increase of the amount of immobilized metal complex should increase their catalytic activity. However, unlike that found with small size carbon disc electrodes, we were unable to increase the amount of immobilized rhodium complex on carbon felt electrodes pre-coated by polyL_1 films synthesized in MeCN electrolyte con-

taining tosylate anions. This behaviour could be attributed to an uneven coating of carbon felt by ligand films. Obviously, additional experiments should be performed with films coated on an electrode with a smooth surface, such as a carbon plate, to try to improve the electrocatalytic activity of the resulting cathodes.

3. Conclusion

The present study confirms that polymer film electrodes functionalized with rhodium(I) and iridium(I) complexes having polypyridyl and diene ligands can be readily synthesized by complexation of $[\text{M}^I(\text{diene})\text{Cl}]_2$ precursor complexes in pre-formed polypyrrole films with pendant polypyridyl ligands. We have also demonstrated that the electropolymerization of a pyrrole-substituted ligand in an electrolyte containing bulky tosylate anions leads to a ligand film characterized by a higher permeability, thus an increased reactivity towards its in situ complexation with a metal centre. The effective complexation was established by cyclic voltammetry and X-ray photoelectron spectroscopy. The resulting polymer modified electrodes allow us to interface these metal complexes with aqueous media. In particular, $[\text{poly}(\text{Rh}(\text{bpy})(\text{COD}))]^+$ films appeared stable enough in these media to perform electrocatalytic reactions such as hydrogen generation and hydrogenation of some α,β -unsaturated ketones. The latter reaction takes place with a different selectivity than that already found with $[\text{Rh}(\text{bpy})_2]^+$ film modified electrodes.

4. Experimental

4.1. Materials and equipment

All electroanalytical experiments were run under an argon atmosphere in a glove-box, using a standard three-electrode electrochemical cell. Potentials are referred to an $\text{Ag}/10^{-2} \text{ M Ag}^+$ reference electrode in MeCN electrolyte, and to a saturated calomel reference electrode (SCE) in aqueous electrolyte. The working electrode was a vitreous carbon disc (0.07 or 0.2 cm^2) polished with 1 μm diamond paste. The electrolyte was a 0.1 M solution of supporting electrolyte in MeCN (Rathburn, HPLC grade S) or DMSO (SDS pure, on 4 Å molecular sieves). The salts tetra-*n*-butylammonium perchlorate (TBAP, recrystallised from dichloromethane-cyclohexane), tetraethylammonium-*p*-toluene sulfonate (TEAS), and tetramethylammonium tetrafluoroborate (TMAF) were obtained from Fluka (puriss), dried under vacuum at 80 °C for 3 days before use, and stored under argon. Electrochemical measurements were carried out using an EG&G PAR model 173 potentiostat equipped with a model 179 digital

coulometer and a model 175 programmer with output recorded on a Sefram TGM 164 X–Y recorder. XPS measurements on polymer films coated on Pt foils ($4 \times 5 \text{ mm}^2$) were performed with a Vacuum Generator ESCA system equipped with a hemispherical analyzer. The excitation source was an Al K α radiation of energy 1486.6 eV. Deconvolution of the experimental spectra was performed using mixed Gaussian/Lorentzian functions. The Rh spectrum was fitted with two groups of double peaks (Rh^I and Rh⁰) and a single peak (Pt). The N spectrum was resolved in two single peaks. The procedures for electrocatalytic hydrogen generation [6] and hydrogenation of unsaturated substrates [7,10] have already been described. GC analysis was performed on a Shimadzu GC-14A equipped with a 0.5 nm molecular sieve column for analysis of hydrogen, or a 20% Carbowax 20 M column for analysis of hydrogenation of organic substrates.

4.2. Ligands, complexes and polymer films

L₁ [29], L₂ [7] and L₃ [6] were synthesized by published methods. The preparation of free ligand films and their complexation with [Rh^I(diene)Cl]₂ precursor complexes have been described in detail elsewhere [11]. For hydrogen evolution and ECH of organic substrates, catalytic cathodes were obtained by coating poly[Rh(L₁)(COD)]⁺ films on carbon felt electrodes (RVC 2000, 65 mg cm⁻², from Le Carbone Lorraine) of dimensions 10 × 10 × 4 mm³. The amount of rhodium complex in the polymer was determined after transfer of the electrode to clean acetonitrile electrolyte, from the charge under the reduction peak of the [Rh^I(L₁)(COD)]⁺/[Rh^I(L₁⁻)(COD)]⁰ redox couple.

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