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Electrochemical and spectroelectrochemical properties of copper(II) Schiff-base complexes

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Abstract

The electrochemical behaviour of several copper(II) complexes with Schiff-base ligands containing pyrrole groups has been investigated in aprotic solvents by cyclic voltammetry and spectroelectrochemistry. Electrochemical oxidation of copper(II) complexes in acetonitrile produces conducting polymeric films at the electrode surface. The modified electrodes were electrochemically and spectrochemically characterized and their electrocatalytical properties have been examined. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Several researches have proposed that the redox potential in macrocyclic and Schiff-base complexes is directly related to many of the biologically relevant chemical characteristics of the entire complex, e.g. dioxygen binding ability and nucleophilicity [1].

Thus, there has been a strong interest in determining thermodynamically meaningful redox potentials of copper Schiff-base complexes and in understanding the relationship between these potentials and the detailed structure of the Schiff-base ligand [2].

Numerous electrochemical studies have been made for a fairly large number of acyclic and macrocyclic copper(II) complexes derived from Schiff-bases. These investigations revealed that the redox properties of copper(II) complexes are markedly influenced by structural and electronic factors [3,4].

Transition metal Schiff-base complexes are interesting due to their capability to form adducts with dioxygen and may thus catalyse dioxygen reduction. The transition metal ions in the complexes form an adduct with dioxygen via charge transfer. These complexes would thus be expected to show catalytic effects [5].

Modified electrodes based on polymeric films of metal complexes are promising electrode materials with many applications [6-11].

The attachment of metal Schiff-base complexes to a polymer matrix is interesting because such systems are relatively easy to prepare and derivatize [12].

The oxidative electropolymerization of various metal-salen complexes has been investigated [13–18].

Dahm and Peters [19] have studied the catalytic reduction of organic halides at carbon electrodes coated with anodically polymerized films of Ni(II)-salen. Recently Choi et al. [20] have studied the electrocatalytic reduction of dioxygen at carbon electrodes modified with Schiff-base Co(II) complexes.

Metal complexes bearing a pyrrole unit are the subject of much current interest because of their use in the production of film-modified electrodes [21]. In previous works we have shown that electropolymerized layers of CoL_2 and NiL_2 (LH: 2-(pyrrol-1-yl-propyliminomethyl)-phenol) exhibit catalytic activity towards the reduction of CO_2 , dioxygen, and alkyl halides and the electro-oxidation of methanol and hydrazine [22,23]. In

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Scheme 1	me I.
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this paper we report the electrochemical behaviour of three Cu(II) Schiff-base complexes bearing pyrrole units (Scheme 1) in connection with structural and electronic factors, and their electro-oxidative polymerization.

2. Experimental

The electrochemical experiments were carried out using either a PAR 362 potentiostat or a BAS CV 27 voltammograph. Data were recorded on a Nicolet 310 digital oscilloscope or a Yokogawa 3025 X - Y recorder. Cyclic voltammetry was performed using a conventional three-electrode system. The working electrodes were pre-polished glassy carbon (GC), gold or platinum discs of area 0.07 cm² (Metrohm). All potentials are expressed versus the saturated calomel electrode (SCE). The surface coverages of the electropolymerized films were determined by integrating the area under the Cu(II)/Cu(I) reduction wave.

Oxygen (pre-saturated with solvent) was bubbled vigorously through the solution for 45 min to ensure saturation. UV–Vis spectra were obtained with a Hewlett–Packard Model 8451A diode array spectrophotometer and a Shimadzu 260 spectrophotometer.

Spectroelectrochemical measurements were made either in a bulk cell [24] with an optical path length of 0.2 cm and a plate of indium tin oxide (ITO)-coated glass as working electrode or in a thin-layer cell with a platinum mesh working electrode.

Table 1 UV–Vis data of the ligands and the Cu(II) complexes

ITO glass electrodes (2 cm^2) covered with electrochemically deposited films were used to obtain in situ UV–Vis spectra of poly-CuL₂ at selected potentials.

X-Band EPR spectra were recorded on a Varian E-12 spectrometer equipped with a HP-5342A frequency meter and Bruker NMR gaussmeter. The ESR studies were performed by using a spectroelectrochemical cell as we described previously [25].

The microstructure of polymer/Au films was examined by scanning electron microscopy (SEM) on a Philips XL-30 instrument.

Acetonitrile was dried over appropriate drying agents and distilled prior to use [26].

Tetra-*n*-butylammonium perchlorate (TBAP), (Fluka) was dried under vacuum at 100 °C before use. Water was purified by passage through a Milli-Q purification train. All other reagents were of at least reagentgrade quality and used as received.

2.1. Compounds

The ligands 2-(3-pyrrol-1-yl-propylimino-methyl)phenol (L¹H), 2-(pyrrol-1-yl-imino-methyl)-phenol (L²H) and 2-(4-pyrrol-1-yl-phenylimino-methyl)-phenol (L³H) and the corresponding Cu(II) chelate complexes CuL₂¹, CuL₂², CuL₂³, were prepared and characterized as described elsewhere [22,27].

3. Results and discussion

3.1. Electronic spectra

The band maxima (λ_{max}) and molar absorptivities (ε) obtained from the electronic spectra of the ligands and complexes are presented in Table 1. In general the UV region of the electronic spectra of these compounds was dominated by intense intra-ligand $\pi - \pi^*$ transitions.

All of the complexes exhibit an absorption band in the range 365-400 nm, which is assigned as an MLCT band. The transitions observed in the visible region (610, 658 and 662 nm) are attributed to weak d-d transitions [28-30].

Compound	λ_{\max} (nm)										
	Intra-ligand and ch	arge transfer			$d \rightarrow d$						
	238 (10 120)	255 (12 640)	316 (4800)								
CuL ¹	246 (47 836)	271 (27 690)	302 (11 818)	365 (12 291)	610 (118)						
L^2	293 (15 460)	302 (16 390)	333 (16 730)								
CuL_2^2	278 (29 360)	293 (32 787)	302 (31 515)	389 (14 121)	658 (167)						
L ³	251 (12 715)	272 (17 258)	345 (16 520)								
CuL ³	250 (51 000)	277 (37 121)	305 (39 364)	397 (21 879)	662 (212)						

Molar absorption coefficient (ε in $1 \text{ mol}^{-1} \text{ cm}^{-1}$) is given in parentheses. Solvent: acetonitrile.

Table 2 IR spectral data for the ligands and their complexes

Compound	<i>v</i> (OH)	ν(CN)	$\delta(OH)$	v(C–O)	v(MO)	ν(MN)
L^1	3097	1629	1365	1276		
CuL_2^1		1612		1328	583	426
L^2	3135	1627	1395	1281		
CuL_2^2		1607		1334	564	431
L ³	3137	1618	1396	1275		
CuL ³ ₂		1606		1329	583	427

Table 3

ESR data for the copper(II) complexes

Compound	g_\parallel	g_{\perp}	$g_{\rm iso}$	$A_{\parallel} \times 10^4 \ ({\rm cm}^{-1})$	$A_{\perp} \times 10^4 \; (\mathrm{cm}^{-1})$	$A_{\rm iso}$	$g_{\parallel}A_{\parallel}^{-1}$ (cm)
CuL ¹	2.239	2.031	2.100	175	24	72	127
$CuL_2^{\tilde{2}}$	2.241	2.046	2.111	171	21	71	130
$CuL_2^{\overline{3}}$	2.246	2.052	2.181	166	19	68	134

3.2. IR spectra

In the IR spectra of the ligands the bands in the 1275–1281 and 1618–1631 cm⁻¹ regions are assigned to v(C=O) and v(C=N), respectively (Table 2). The v(C=N) band of the ligands undergoes small shifts to lower frequencies in the spectra of the complexes (1606–1612 cm⁻¹) indicating coordination of the imine nitrogen [31,32]. Additional evidence for coordination of nitrogen is the presence of the v(M-N) band in the 426–431 cm⁻¹ range.

The coordination through the oxygen atom is inferred from the shifts to lower wavenumbers of the v(C-O) band as compared to the position in the ligands [31] and the appearance of a new band in the 564–583 cm⁻¹ region, assigned to v(M-O), in agreement with the literature [33,34].

3.3. ESR spectra

In frozen CHCl₃ solution the copper complexes show axial spectra, the *g* factors and *A* constants are summarized in Table 3. The data for both *g* and *A* are indicative of a predominantly $d_{x^2-y^2}$ ground state with D_{4h} symmetry. The order $g_{\parallel} > g_{\perp}$ and $A_{\parallel} > A_{\perp}$ is found for all complexes studied.

It is well known that a pseudo-tetrahedral distortion leads to a greatly reduced value of A_{\parallel} and an increased value of g_{\parallel} . Often the ratio $g_{\parallel}/A_{\parallel}$ has been empirically treated as an index of tetrahedral distortions; for square-planar structures the usual range is 105–135 and for tetrahedral distorted complexes it is 150–250. The values obtained in our case, 125–135, indicate the absence of tetrahedral distortion of the CuN₂O₂ plane in the complexes [35]. The small decrease in the data for A in the order $CuL_2^1 > CuL_2^2 > CuL_2^3$ indicates a slightly increasing electron-withdrawing effect of the substituents which causes a slightly lowered density of the unpaired electron on the copper [35].

3.4. Electrochemistry

The behaviour of CuL_2^1 is depicted in Fig. 1 and is similar to that found for all copper complexes. On the negative scan, two well-defined reduction peaks, I and II, are formed whereas, on the reverse sweep, up to three oxidation peaks, I', A and B can be observed (Fig. 1(a)). If the cathodic scan is limited to the first reduction peak a quasi-reversible redox couple I/I' ($E_{1/2} =$ -0.86 V) is only observed. This first reduction process is diffusion controlled with the cathodic current function ($I_{pc}/v^{1/2}$) independent of the scan rate (v) over the range 0.01–0.5 V s⁻¹. The peak potentials separation is $\Delta E_p = 80$ mV and the ratio of cathodic to anodic peak current is close to unity. Controlled potential electrolysis revealed that a single electron is involved in this first reduction step.

The second cathodic step, II, with $E_p = -1.72$ V, is totally irreversible at all sweep rates in the range 0.01–1 V s⁻¹. The peak potential $E_p(II)$ shifts cathodically on increasing the scan rate with a variation of approximately 48 mV for each tenfold increase in v, and the peak width at half-peak, $(E_p - E_{p/2})$, is approximately 70 mV, whereas the peak current $I_p(II)$ is approximately equal to that of the first reversible one-electron peak I.

When the potential scan is reversed back at -2.0 V in the positive direction significant changes on the anodic response can be observed, appearing two new oxidation peaks (A and B).





Fig. 1. Cyclic voltammograms of 1 mM CuL_2^1 at a glassy carbon electrode in acetonitrile, 0.1 M TBAP, scanning to cathodic and anodic potentials for curves (a) and (b), respectively. Scan rate: (—) 100; (---) 50 mV s⁻¹.

The cyclic voltammogram for the electro-oxidation of CuL₂¹, shows three irreversible anodic waves at + 1.10 V (peak III), +1.18 V (peak IV) and +1.56 V (peak V) (Fig. 1(b)). Peaks III and V are observed at nearly the same potential values as the corresponding ligand (HL¹) and can be attributed to the irreversible oxidation of the pyrrole and the Schiff-base groups, respectively [16,23].

Wave IV, which is absent in the CV of the free ligand, can be associated to the irreversible oxidation of Cu(II) to Cu(III). The electrochemical response of the

Table	4	
Cyclic	voltammetric	data



Fig. 2. Cyclic voltammogram of 1 mM CuL_2^1 at a Pt electrode in acetonitrile, 0.1 M TBAP. Scan rate: 100 mV s $^{-1}.$

complexes CuL_2^2 and CuL_2^3 are essentially the same with minor shifts in the potential values (Table 4).

The features found in the electroreduction of CuL_2^1 are consistent with an irreversible chemical reaction following the quasi-reversible acquisition of one electron in the second cathodic wave.

The dissociation to elemental copper of the dianion species is confirmed by running the cyclic voltammogram in the positive direction up to +2.0 V. In fact only two peaks appear at potentials corresponding to the free ligand species liberated after the decomposition of the reduced form at -1.8 V (Fig. 2).

This observation is confirmed by recording the cyclic voltammogram of Cu(ClO₄)₂, 10^{-3} M in CH₃CN/TBAP. The results obtained allow to ascribe peak A at -0.48 V to the Cu⁰ \rightarrow Cu²⁺ + 2e⁻ redox process and peak B at -0.28 V to the Cu⁰ \rightarrow Cu⁺ + e⁻ transfer [31].

The electrochemical reduction response of CuL_2^3 at Pt, GC electrodes is similar to that found for CuL_2^1 with considerable shifts in the potentials, and which is more important with the absence of peaks A and B.

This absence of the anodic peaks A and B in the cyclic voltammogram indicates that no decomposition of the reduced species occurs in the time-scan cyclic voltammetry.

Similar to the other compounds, CuL_2^2 also undergoes two one-electron reduction steps. Peak I, observed at -0.58 V in the cathodic sweep, shows its counter-

Compound	Reduction			Oxidation				
	$\overline{E_{\rm pc}({\rm I})}$	$E_{\rm pa}({\rm I}')$	$E_{\rm p}({\rm II})$	$E_{\rm p}({\rm A})$	$E_{\rm p}({\rm B})$	$E_{\rm pa}({\rm III})$	(IV)	(V)
CuL ¹ ₂	-0.90	-0.82	-1.72	-0.48	-0.28	+1.10	+1.28	+1.56
CuL ² ₂	-0.58	-0.34	-1.02			+1.20	+1.58	+1.75
CuL_2^3	-0.60	-0.50	-1.60			+1.23	+1.54	+1.70

Compounds: 1 mM in acetonitrile; 0.1 M TBAP. Scan rate 100 mV s⁻¹; E values (V vs. SCE). E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.

part in the reverse scan at -0.34 V. The electrochemical process is diffusion controlled with $I_p/v^{1/2}$ constant in the range 10–500 mV s⁻¹ and the ratio of cathodic to anodic peak current is close to unity. The peak-topeak separation, $\Delta E_p = 240$ mV, is considerably greater than those found for CuL₂¹ and CuL₃², suggesting a quasi-reversible charge-transfer.

In this case the large oxidation peak B, characteristic of the dissolution of elemental copper electrodeposited, occurs only at low scan rates or after holding the potential at -1.8 V.

Fig. 3 shows the changes of the electronic spectrum of CuL_2^2 that accompany the reduction process. A well-defined isosbestic point is observed at $\lambda = 352$ nm, confirming that the electrode reaction proceeds in a quantitative fashion and therefore the absence of any coupled chemistry.

The metal to ligand charge transfer (MLCT) at 380 nm decreases and a relatively strong peak at 327 nm develops [29]. In addition, a weak band at 646 nm appears in the expected d-d transition region for the Cu(II) complexes.



Fig. 3. Absorption spectra of 0.3 mM CuL_2^2 in acetonitrile, 0.1 M TBAP. Applied potentials: (a) initial spectrum; (b) -0.9 V; (c) -1.0 V; (d) -1.1 V; and (e) -1.2 V vs. SCE.



Fig. 4. Absorption spectra of 0.3 mM CuL_2^1 in acetonitrile, 0.1 M TBAP. Applied potentials: (a) initial spectrum; (b) -1.0 V; (c) -1.25 V; and (d) -1.5 V vs. SCE.

This spectroelectrochemical response is different from that displayed by the CuL_2^1 compound during the reduction process (Fig. 4). In this case, the absorption maximum at 305 nm decreases and an intense absorption band centred at 384 nm develops, which is attributed to an MLCT transition in Cu(I) complexes [28]. These changes are in agreement with the expected results for a metal-centred reduction Cu(II) \rightarrow Cu(I) [36,37].

On the contrary, the spectroelectrochemical behaviour shown by CuL_2^2 , described above is indicative of a ligand-centred reduction, the added electron will lie in molecular orbitals centred mainly in the ligands and this complex should be formulated as Cu(II) with stabilized ligand anion radicals.

A similar behaviour has been previously found for the electro-reduction of other copper quelate complexes containing the O_2N_2 donor set [38].

It has been shown that in the case of copper complexes with identical stereochemistry the potentials of metal-centred redox process are affected by the electronic properties of the substituents [3,4].

In accordance with the ESR data in the case of the complexes studied, the reduction potentials (E_p) would be shifted to more negative values in the order $\text{CuL}_2^3 < \text{CuL}_2^2 < \text{CuL}_2^1$, which is consistent with the increase in the electron-donating ability of the substituents.

Nevertheless, the results obtained show that the first reduction step of CuL_2^2 occurs at a potential slightly more positive than that exhibited by CuL_2^3 . This behaviour can be due to a ligand-centred reduction and also to structural features.

It has been established that the electrochemical properties of the copper complexes are also related with changes in the flexibility of the coordination spheres [3]. Thus, a change from planar to tetrahedral configuration in the reduced complexes enhances their stability and produces anodic shifts in the reduction potentials [3]. This effect is observed for the complex CuL_2^2 . The large departure from electrochemical reversibility observed in the first reduction step of CuL_2^2 , $\Delta E_p = 240$ mV, indicates that a geometrical reorganization, hindered to a large extent by the low flexibility of the coordination sphere, is involved in the reduction process.

In the quasi-reversible reduction, ($\Delta E_p = 100 \text{ mV}$), of CuL₂³ complex this geometrical reorganization is probably prevented by the presence of a more rigid coordination sphere [35].

In general, the three copper complexes undergo an electro-oxidatively initiated polymerization which gives rise to electrodes modified with an electroactive polymer film of the compound.

The thin polymeric films formed adhere strongly to GC, Pt and Au electrodes. The electrochemical data for the films obtained from the different copper(II) com-

		~								
Electrochemical	data	for	the	electro	oolv	merized	films	of	copper	complexes

Compound	Potential range ^a for electro- polymerization (V vs. SCE)	Apparent molar coverage $\tau_{\rm app} \ ({\rm mol} \ {\rm cm}^{-2})$	Reduction		Reduction		Oxidation	Apparent diffusion coefficient D (cm ² s ⁻¹)
			$E^{0\prime}$ (V)	$\Delta E_{\rm p}~({\rm mV})$	$E_{\rm pa}$ (V)	-		
CuL ¹ ₂	0.0-+1.6	4.0×10^{-9}	-1.01	35	+0.87	0.13×10^{-10}		
CuL_2^2	0.0 - +1.75	2.4×10^{-8}	-0.85	100	+0.87	0.57×10^{-10}		
CuL ³ ₂	0.0 - +1.75	2.7×10^{-8}	-0.81	120	+0.95	0.60×10^{-10}		

^a Acetonitrile/0.1 M TBAP was used to study the electropolymerization and electrochemistry of films.

plexes are listed in Table 5. Fig. 5(a) shows the evolution of the cyclic voltammograms of CuL_2^1 complex in acetonitrile solution, during repeated potential scans between 0.0 and + 1.6 V.

Oxidation of the monomer is observed during the first positive scans. In the subsequent scans the current decreases and after some cycles the initial oxidation peaks disappear and a new peak appears at +1.5 V. After deposition, the electrode was rinsed and transferred to a fresh monomer-free electrolyte solution. The cyclic voltammogram of this modified electrode displays a well-defined system at $E_{1/2} = -1.01$ V (Fig. 5(b)); which can be ascribed to the Cu(II)/Cu(I) process. The ΔE_p value increases with film thickness, however, at low coverages (<3.7 × 10⁻¹⁰ mol cm⁻²) it remains equal to 35 mV and is independent of v (over the range 10–500 mV s⁻¹).

The peak current tends to vary with v at slow scan rates ($v < 100 \text{ mV s}^{-1}$) and with $v^{1/2}$ at high scan rates.

The orange films of poly- CuL_2^1 formed were insoluble in common organic solvents and exhibit a high stability towards electrochemical cycling between the Cu(II) and Cu(I) states. After 20 scans between 0.0 and -1.8 V a steady state is reached with negligible loss of the complex activity.

Spectral measurements were used to characterize the film on an optically transparent electrode ITO-coated glass electrode.

Fig. 6 shows the optical absorption spectra of a poly-CuL₂¹ film, deposited by cycling between 0.0 and + 1.6 V, when different potentials are applied.

The same pattern of absorption bands was observed in polymeric films as for the monomer CuL_2^1 in solution with only slight shifts of the λ_{max} values between the solution phase and the film environment.

The peak at 311 nm is shifted to lower energies and the absorption in the 370–390 nm region increases as the electrode potential becomes more negative.

Both CuL_2^2 and CuL_2^3 can similarly be electro-oxidatively polymerized onto the surface of an electrode by cycling the applied potential between 0.0 and +1.75 V. Electrochemical polymerization of these compounds can be also achieved by controlled potential electrolysis at +1.7 and +1.5 V, respectively. In the 0.0 to -1.0 V region the CV of electrodes modified with poly-CuL₂² and poly-CuL₂³ exhibit redox systems at $E_{1/2} - 0.85$ and -0.81 V, respectively, that could be attributed to the Cu(II)/Cu(I) process.

Plots of cathodic peak current against sweep rate were linear for thin films ($\tau = 5 \times 10^{-10} \text{ mol cm}^{-2}$).

Such behaviour is expected for a surface-inmobilized electroactive film. As the film thickness increases, deviation from linearity was more pronounced and occurred at slower sweep rates, indicating that the electrochemical response becomes progressively diffusion dependent.



Fig. 5. (a) Consecutive cyclic voltammograms of 1mM CuL₂¹ in acetonitrile, 0.1 M TBAP at a gold electrode; scan rate = 100 mV s⁻¹. (b) Cyclic voltammogram of a gold electrode coated with a film of poly-[CuL₂¹] ($\tau = 3.7 \times 10^{-10}$ mol cm⁻²) in acetonitrile, 0.1 M TBAP; scan rate = 100 mV s⁻¹.



Fig. 6. Electronic absorption spectra of a poly-[CuL¹₂] film on an ITO electrode in acetonitrile, 0.1 M TBAP. Applied potentials: $(- \times -)$ initial spectrum; $(\times \times \times) - 1.0$ V and (--) - 1.5 V vs. SCE.



Fig. 7. Scanning electron micrograph of poly- $[CuL_2^2]$ film deposited electrochemically on a gold foil electrode at a constant potential of + 1.7 V.



Fig. 8. Scanning electron micrograph of poly-[CuL $_{2}^{l}$] film deposited electrochemically on a gold foil electrode by cycling from 0.0 to + 1.6 V.

Potential-step chronoamperometry was used to determine the apparent diffusion coefficient D for charge transport. Several films of the copper compounds, deposited onto platinum electrodes were examined individually.

Reproducible plots of current versus $t^{1/2}$ were obtained for different films upon application of a -0.5 to -1.25 V potential step and the slope of the linear portion of the plot was measured.

The respective products $D^{1/2}C$ were calculated from the Cottrell equation by analysing the linear portion of the plots. The values of *D* obtained (Table 5), assuming a redox site concentration, *C*, of 10^{-3} mol cm⁻³, are in close agreement with that determined for other electrochemically polymerized films of pyrrole-metal Schiffbase monomers [23].

Scanning electron microscopy demonstrated that the films' morphology is slightly different.

A scanning electron micrograph of poly- CuL_2^2 (Fig. 7) grown at a constant potential +1.7 V on a gold electrode shows a compact structure and a relatively smooth surface. A similar surface morphology was also obtained for a film of the poly- CuL_2^3 film.

Contrary to this, the surface of a poly- CuL_2^1 film, obtained by cycling between 0.0 and + 1.6 V, (Fig. 8) is rougher than the surface observed for poly- CuL_2^2 and poly- CuL_2^3 . It presents a less compact morphology and a poor porosity can be detected at high magnifications.

3.5. Catalysis studies

Electrodes modified with films of electropolymerized CuL_2^1 exhibit electrocatalytic activity towards the reduction of oxygen. Fig. 9 shows the voltammetric response for a bare and poly-CuL₂¹ modified Au-electrode ($\tau = 4 \times 10^{-9} \text{ mol cm}^{-2}$) in an oxygen-saturated 0.1 M NaOH solution. At the poly-CuL₂¹ modified electrode, the potential for the electrochemical reduction of oxygen is shifted anodically 400 mV, relative to the potential at the bare electrode, indicating clearly a lowering of the activation energy for that reaction.

of the activation energy for that reaction. The slope of i_p/A versus $v^{1/2}$ is 2.4 mA cm⁻² (V/s)^{1/2}, slightly less than the theoretical value of 3.2 for the optimal catalytic reduction of dioxygen directly to water [39].

Voltammetric measurements with a rotating ring-disc electrode (a gold disc covered with the polymeric film and a platinum ring) indicate the presence of small amounts of hydrogen peroxide. These results suggest the presence of a parallel catalysis pathway in which O_2 is reduced to H_2O_2 instead of to H_2O .

The poly- CuL_2^1 electrode was also shown to catalyse the reduction of oxygen in an acid solution. Fig. 10 depicts the voltammetric response for a bare gold electrode and a gold electrode modified with poly- CuL_2^1 in 0.1 M H₂SO₄. It is evident from the significant current enhancement (by about 58.2%) observed at -0.34 V, that electrodes modified with electropolymerized films of CuL₂¹ exhibit a significant electrocatalytic activity toward the reduction of O₂.

It should be noted that the potentials for the reduction of O_2 are nearly the same in acid and alkaline solutions. This fact suggests that the rate-determining step in the mechanism of oxygen reduction is the formation of superoxide which is pH independent [40,41].

This may directly be reduced to H_2O_2 or to H_2O as a stable end product depending on the way the oxygen is adsorbed onto the catalyst, involving in each case a different number of metal-atoms in the interaction with the O_2 molecule [42].

These preliminary studies indicate the potential application of electrodes modified with these polypyrrole Cu(II) Schiff-base complexes in the field of catalysis.



Fig. 9. Cyclic voltammograms at 100 mV s⁻¹ for: (a) a bare gold electrode; and (b) a gold electrode coated with a film of poly-[CuL¹₂] ($\tau = 4 \times 10^{-9}$ mol cm⁻²) both in 0.1 M aqueous NaOH solution saturated with oxygen.



Fig. 10. Cyclic voltammograms at 100 mV s⁻¹ for: (a) a bare gold electrode; and (b) a gold electrode coated with a film of poly-[CuL¹₂] ($\tau = 4 \times 10^{-9}$ mol cm⁻²) both in 0.1 M aqueous H₂SO₄ solution saturated with oxygen.

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