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Electrocatalytic reduction of CO_2 and O_2 with electropolymerized films of vinyl-terpyridine complexes of Fe, Ni and Co

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Abstract

We have prepared and characterized, by cyclic voltammetry in acetonitrile and DMF (under N_2 or CO_2) for CO_2 reduction, and in aqueous media for O_2 reduction, iron, nickel and cobalt complexes of a terpyridine (tpy) and vinyl-terpyridine (v-tpy). These materials exhibit electrocatalytic activity towards the reduction of CO_2 and the magnitude of the catalytic effect is a function of the metal center. In the case of electropolymerizable metal complexes (those incorporating v-tpy) electrodeposited films exhibited higher electrocatalytic activity than the corresponding tpy complexes in solution. In the case of electropolymerized films of $[Fe(v\text{-}tpy)_2]^{2+}$, electrocatalysis for CO_2 reduction was observed at potentials below -1.0 V which represents a very significant diminution (of about 1 V) in the overpotential. In the case of oxygen, the electrocatalytic activity of the electropolymerized films as well as the predominant product (peroxide or water) was dependent on the surface coverage.

Keywords: Electrocatalysis; Reduction of carbon dioxide; Reduction of oxygen; Cyclic voltammetry; Iron complexes; Vinyl-terpyridine complexes

1. Introduction

Because of their abundance in the atmosphere and the increasing need for new sources of fuels, there has been, in the recent past, much interest in the design of electrocatalysts for the reduction of carbon dioxide [1] to useful fuel products as well as for the four-electron reduction of oxygen to water. These reactions are particularly difficult to catalyze since they not only involve multiple electron transfers but because they are also often coupled to chemical steps such as protonation. Furthermore, there can be multiple competing reaction pathways giving rise to a variety of reaction products. The two-electron reduction of oxygen to peroxide is an undesirable reaction that often dominates the four-electron reduction to water. The reduction of carbon dioxide can also give rise to a variety of products including carbon monoxide, formic acid, methanol and methane among others as shown below:

	$E°$ (V) vs. NHE	
$CO_2 + 2H^+ + 2e^- \longrightarrow HCO_2H$	-0.61	(1)
$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$	-0.52	(2)
$CO_2 + 4H^+ + 4e^- \longrightarrow HCHO + H_2O$	-0.48	(3)
$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$	-0.38	(4)
$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$	-0.24	(5)

These potentials represent thermodynamic values for these reactions. Experimentally, the reduction of carbon dioxide at a platinum electrode requires much more negative potentials (-2.0 V versus SSCE in DMF solution) because of the formation of high energy intermediates such as CO_2^{1-} [2].

The large activation energy for the formation of CO_2^{1-} has been circumvented through the use of a variety of catalysts such as semiconductor electrodes and transition metal electrocatalysts [3]. A number of transition metal complexes have been shown to be effective in the electrocatalytic reduction of carbon dioxide. For example, Co and Ni tetraazamacrocycles [4], which were initially reported by Fisher and Eisenberg [5], were found to diminish the potential for carbon dioxide reduction by about 0.5 V. The complex $Ni(cyclam)^{2+}$ (cyclam is 1,4,8,11-tetraazatetradecane) has been used as an electrocatalyst in aqueous media [6]. Other types of complexes that have been studied are phthalocyanine and porphyrin complexes [7], phosphine complexes [8] such as $Rh(diphos)_2Cl$ [9] (diphos is 1,2-bis(diphenylphosphino)ethane) and polypyridyl-type transition metal complexes [10]. In most of these cases, the catalyst is capable of undergoing more than

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one reduction and thus storing multiple redox equivalents. In addition, in most cases, the catalyst has at least one open coordination site available after reduction where carbon dioxide can ostensibly bind.

In addition to utilizing electrocatalysts in solution, there have been a number of reports on the use of electrodes modified with immobilized electrocatalysts [11]. The use of surface-bound catalysts presents a number of advantages. First, the effective concentration of electroactive material can reach levels (~0.5 M) that cannot be attained in homogeneous solution. Furthermore, at such high concentrations, the short distance between adjacent metal complexes enhances cooperativity effects between the transition metal units. Another advantage of using surface-immobilized electrocatalysts in the ease with which the catalyst can be removed from the reaction vessel.

One important type of surface-bound electrocatalyst used for CO_2 reduction has been metallophthalocyanines deposited onto glassy carbon electrode surfaces. For example, cobalt phthalocyanines immobilized in this manner have been shown to reduce carbon dioxide to carbon monoxide at potentials as low at -0.65 V versus SCE at pH 5 [12].

Another method used for immobilizing catalysts onto electrode surfaces has been through the use of complexes containing polymerizable, vinyl substituted ligands. Electropolymerization of $[Re(CO)_3(v\text{-}bpy)Cl]$ (v-bpy is 4-vinyl-4′-methyl-2,2′-bipyridine) gives rise to the formation of polymeric films which adhere to the electrode surface and remain electroactive. Platinum electrodes modified with polymeric films of $[Re(CO)_3(v\text{-}bpy)Cl]$ can reduce carbon dioxide to carbon monoxide electrocatalytically [13].

Electropolymerized films of $[Co(v\text{-}tpy)_2]^{2+}$ (v-tpy is 4′-vinyl-2,2′:6′,2″-terpyridine) are also electrocatalytically active in the reduction of carbon dioxide to formic acid and of oxygen to water and hydrogen peroxide [14]. In DMF solution, $Co(tpy)_2{}^{2+}$ (tpy is 2,2′:6′,2″-terpyridine) can reduce carbon dioxide at -1.70 V. However, electrodes modified with polymeric films of $[Co(v\text{-}tpy)_2]^{2+}$, can reduce CO_2 under similar conditions at -0.9 V. This difference in reactivity appears to be the result of the generation of empty coordination sites on the cobalt once it is reduced to Co(I) and possibly to cooperativity effects.

For the oxygen reduction reaction, electropolymerized films of $[Co(v\text{-}tpy)_2]^{2+}$ catalyzed both the two-electron reduction to hydrogen peroxide as well as the four-electron reduction of oxygen to water. At low polymer coverages only the two-electron reduction to peroxide was favored, whereas at high coverages, both processes were observed. Given the fact that in this given regime polymer density increases with coverage, this mechanistic difference was regarded as evidence for cooperativity effects between adjacent metal containing units within the polymeric film. Since the reduction of oxygen to water requires the simultaneous transfer of four electrons, the shorter metal–metal distances achieved in polymers with high coverages appeared to favor this reaction pathway over the two-electron reduction to peroxide.

In terms of other materials immobilized on electrode surfaces, the now classic work of Anson and co-workers [15] represents one of the most elegant examples of not only oxygen reduction, but of electrocatalysis at chemically modified electrodes in general. They employed a family of dicobalt face-to-face porphyrins where the length of the link between the two porphyrins was systematically varied. These were adsorbed onto pyrolytic graphite electrodes and their electrocatalytic activity assessed. In one of the more dramatic cases, the onset of cathodic current was about +0.80 V with virtually no peroxide generated.

Anson and Chang [16] have also employed so-called 'pac-man' porphyrins. These have the advantage of synthetic simplicity.

Collman and Kim [17] showed that a monomeric Ir porphyrin was capable of the four-electron reduction of O_2.

Anson and co-workers have also employed adsorbed Cu [18] and Ni [19] complexes in the reduction of O_2. Most recently, they have employed ruthenated porphyrins [20] as very effective catalysts.

From previous findings, it was clear that any potential electrocatalyst had to meet a number of requirements. First, the complexes had to be stable enough for preparation, isolation and purification. However, they had to be reactive enough so that upon reduction they could generate an empty coordination site needed for binding by carbon dioxide or oxygen molecules. For these reasons, this investigation concentrated on the first row transition metals Fe(II), Co(II) and Ni(II).

In addition, we have previously found that with the use of terdentate ligands [21], the reactivity associated with the first row transition metals can still be exploited while maintaining the overall stability of the metal complex. With this in mind, we have prepared vinylterpyridine complexes of Fe, Co and Ni which can be electropolymerized and we have, additionally, determined their electrocatalytic activity towards the reduction of CO_2 and O_2 and compare these results with those for the tpy complexes in homogeneous solution.

2. Experimental

The ligand 2,2′,6′,2″-terpyridine (Aldrich Chemical Company) was used as received. The ligand 4′-vinyl-2,2′,6′,2″-terpyridyl was prepared according to literature methods [14].

Electrochemical measurements were performed in acetonitrile, dimethyl formamide, (Burdick & Jackson distilled in glass, dried over 4 Å molecular sieves) or water (purified by passage through a Milli-Q purification system).

For non-aqueous solvents (acetonitrile, DMF) the supporting electrolyte was tetrabutylammonium perchlorate (TBAP) (G.F.S. Chemicals, recrystallized three times from ethyl acetate and dried under vacuum for 72 h). In aqueous media, potassium perchlorate (Aldrich, recrystallized from water) or sodium perchlorate (Aldrich, used as received) were employed. Buffer systems employed in studies of the electrocatalytic reduction of oxygen were acetate, phosphate or borate.

All other reagents were at least of reagent grade quality and were used as received.

2.1. Syntheses

2.1.1. $[M(L)_2]^{2+}(PF_6)_2$ (M=Fe, Co; L=tpy, v-tpy)

These complexes were prepared by mixing degassed aqueous solutions of the chloride salt of the metal ion with 2.3 equiv. of the ligand. Complex formation was immediately apparent from the resulting color changes. The solution was allowed to stir at room temperature for 30 min. The complexes were precipitated by the addition of an aqueous, saturated solution of ammonium hexafluorophosphate. The complexes were collected by filtration, washed and dried with diethyl ether and recrystallized from acetone/ether.

2.1.2. $[Ni(L)_2]^{2+}(PF_6)_2$ (L=tpy, v-tpy)

$NiCl_2 \cdot 6H_2O$ was combined with 2.3 equiv. of the ligand in 1:1 ethanol/water. The solution was vigorously bubbled with pre-purified nitrogen for 20 min, and heated at reflux for 3 h. The dark yellow solution was allowed to cool and filtered to remove any unreacted terpyridine. Upon addition of an aqueous, saturated solution of ammonium hexafluorophosphate, a white precipitate formed and was collected by filtration. The product was washed with diethyl ether and recrystallized from acetone/ether.

Typical yields for all of the complexes prepared, after purification, were in the range 70–90%.

Ligands and transition metal complexes were characterized by elemental analysis, which was performed by Quantitative Technologies Inc., Bound Brook, NJ and/or by fast atom bombardment mass spectrometry on either a Kratos MS-890 or a VG ZAB-SE spectrometer using 3-nitrobenzyl alcohol as matrix.

2.2. Techniques

Electrochemical experiments were performed using either a platinum disk working electrode ($A = 0.008$ cm^2) sealed in glass, a glassy carbon disk electrode ($A = 0.045$ cm^2), or a rotated-ring–disk electrode (Pine Instruments) with a glassy carbon disk ($A = 0.283$ cm^2) and a platinum ring. The electrodes were polished prior to use with 1-μm diamond paste (Buehler) and rinsed thoroughly with water and acetone.

Potentials are referenced to a saturated sodium calomel electrode (SSCE) (+0.241 V versus NHE) or a Ag/AgCl (saturated with sodium chloride) (+0.222 versus NHE) electrode. A coiled platinum wire was used as counter electrode and electrochemical cells were of conventional design.

Solutions for electrochemistry were typically millimolar in the redox species and were deoxygenated by purging with pre-purified nitrogen for at least 20 min. Unless otherwise stated, the sweep rate in cyclic voltammetric experiments was 100 mV s^{-1}.

The electrochemical instrumentation utilized was either a Pine Instrument Company electrochemical analyzer model RDE3 or a PAR model 173 potentiostat in conjunction with a PAR model 179 universal programmer. Data were recorded on a Soltec model VP-6423S recorder.

Spectrophotometric measurements were carried out on a H-P model 8451A diode array spectrophotometer.

Electropolymerization of the v-tpy complexes was carried out in acetonitrile as previously described [14]. The surface coverage was controlled depending on the desired value.

The electrocatalytic activity of the metal complexes towards the reduction of carbon dioxide was tested by comparing their voltammetric response under an atmosphere of nitrogen and carbon dioxide, respectively. In order to ensure that the solution was saturated with CO_2, the solution was vigorously bubbled for at least 30 min with a solvent saturated stream of CO_2. In all cases, after the voltammetric response of the complex in a carbon dioxide atmosphere was obtained, the solution was purged with nitrogen and the cyclic voltammogram obtained again to ensure that it was identical to that before the CO_2 experiments. In these studies, DMF was used as a solvent since acetonitrile can behave as a moderately strong coordinating solvent.

The detection and quantification of the reduction products from the reduction of CO_2 (formate and formaldehyde) was through the chromotropic acid test [22].

For the electrocatalytic activity of O_2 reduction, aqueous solutions of different pH were vigorously bubbled with a solvent saturated stream of O_2 for at least 30 min. In order to prevent complications due to hydrogen evolution, a glassy carbon working electrode was employed in these studies. In order to test for peroxide formation, a glassy carbon disk/platinum ring electrode was employed. The potential of the platinum ring was held at +0.80 V in order to ensure that any peroxide generated was consumed at a mass transport limited rate.

3. Results and discussion

3.1. *Preliminary electrochemical characterization of tpy complexes*

Since the electrochemical behavior of these complexes is relatively well known [23], only a brief description is given. This is then followed by a discussion of the behavior of electropolymerized films. In general, the terpy complexes exhibited both metal localized as well as ligand localized processes. For the iron complexes [23,24], typically one metal based redox process was observed. The cobalt [25] and nickel [26] complexes, as anticipated, exhibited two metal based redox processes. In addition, all the complexes exhibited ligand localized reductions. Table 1 presents a compilation of the electrochemical data determined by cyclic voltammetry in acetonitrile (CH_3CN)/0.1 M TBAP. All redox processes involve one-electron transfers unless otherwise indicated.

All of the complexes tested exhibited some electrocatalytic behavior towards the reduction of carbon dioxide. The last column on Table 1 lists the potentials at which the electrocatalytic reduction of carbon dioxide (in DMF/0.10 M TBAP) took place for the various complexes. In this Table, the values reported represent the potential of the wave at which the first current enhancement due to the electrocatalytic reduction of carbon dioxide was observed. Although the potential at which carbon dioxide was catalytically reduced varied for the various complexes, all the complexes exhibited some degree of electrocatalytic activity. In addition, a number of the complexes exhibited electrocatalytic behavior for potentials positive of −1.00 V, indicative of a very strong electrocatalytic effect since the reduction of carbon dioxide in DMF/0.1 M TBAP in the absence of the complexes takes place at potentials more negative than −2.0 V. The specific systems are described below.

Table 1
Redox potentials vs. SSCE for Fe, Co and Ni complexes of tpy and v-tpy at a platinum electrode in CH_3CN/0.10 M TBAP and the potential for the electrocatalytic reduction of CO_2 in DMF/0.10 M TBAP

Complex	Solvent	$E°$ (V)	ΔE_p (mV)	E_{red} (CO_2) (DMF)[a]
$Fe(tpy)_2(PF_6)_2$	CH_3CN	+1.10	[70]	−1.13
		−1.13	[70]	
		−1.27	[60]	
		−1.94	[70]	
$Co(tpy)_2(PF_6)_2$	CH_3CN	+0.27	[60]	−1.56
		−0.77	[70]	
		−1.56	[60]	
		−1.91	[60]	
$Ni(tpy)_2(PF_6)_2$	CH_3CN	+1.65	[60]	−1.20
		−1.20	[80]	
		−1.38	[70]	
$Fe(v\text{-}tpy)_2(PF_6)_2$	CH_3CN	+1.04	[80]	−0.95
		−1.19	[80]	
		−1.38	[70]	
		−1.94	[70]	
$Co(v\text{-}tpy)_2(PF_6)_2$	CH_3CN	+0.26	[60]	−0.90
		−0.79	[60]	
		−1.70	[60]	
$Ni(v\text{-}tpy)_2(PF_6)_2$	CH_3CN	+1.62	[110]	−1.22
		−1.25	[80]	
		−1.45	[80]	

[a] DMF was employed since it is a non-coordinating solvent.

3.1.1. *$Co(tpy)_2(PF_6)_2$*

It has been previously shown that, in DMF solution, $Co(tpy)_2(PF_6)_2$ can catalyze the reduction of carbon dioxide [14]. In DMF/0.1 M TBAP solution, $Co(tpy)_2(PF_6)_2$ exhibits two one-electron metal based reductions with formal potentials of +0.27 and −0.77 V corrcsponding to Co(III/II) and Co(II/I) processes, respectively. In addition, the complex exhibits two ligand based reductions at −1.56 and −1.91 V. The electrocatalytic reduction of CO_2 is observed as an enhancement of the current (relative to the current under an atmosphere of nitrogen) at the ligand based process at −1.56 V by 95% and an even greater enhancement (820%) at the redox process at −1.91 V. One of the major reduction products from this catalytic process is formate as determined from the product analysis (via the chromotropic acid test) following controlled potential electrolysis experiments at −1.70 V and after passing over 4 equiv. of charge/Co center. Such behavior has been previously reported [14].

3.1.2. *$Ni(tpy)_2(PF_6)_2$*

The analogous nickel complex, exhibited two metal based redox processes at +1.65 and −1.20 V corresponding to the Ni(II/III) and Ni(II/I) redox couples. The complex showed one additional reduction at −1.38 V which is ligand based. These assignments were made based on analogous nickel complexes as well as on the electrochemical experiments described in the next section for the electropolymerizable complex $Ni(v\text{-}tpy)_2(PF_6)_2$. Fig. 1 shows the cyclic voltammogram in DMF/0.1 M TBAP of $Ni(tpy)_2(PF_6)_2$ under nitrogen and carbon dioxide atmospheres. It is evident from the significant current enhancement (by 267%) observed at the metal based redox process at −1.20 V that $Ni(tpy)_2(PF_6)_2$ exhibits a strong catalytic effect for the reduction of CO_2. This represents a diminution in the overpotential for carbon dioxide reduction of about 0.8 V.

3.1.3. *$Fe(tpy)_2(PF_6)_2$*

$Fe(tpy)_2(PF_6)_2$ exhibits only one metal based redox proccss with a formal potential at +1.10 V which corresponds to the Fe(II/III) oxidation. In the negative

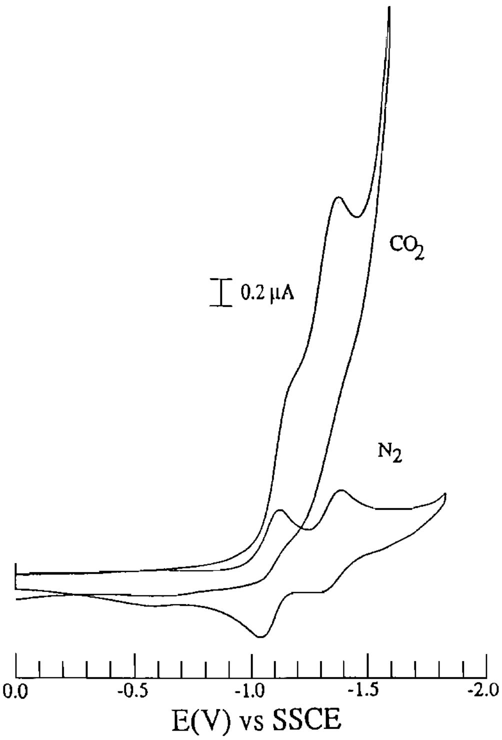

Fig. 1. Cyclic voltammogram of $Ni(tpy)_2(PF_6)_2$ at 100 mV s^{-1} in 0.10 M TBAP/DMF solution under nitrogen and carbon dioxide atmospheres, respectively.

potential region, $Fe(tpy)_2(PF_6)_2$ exhibits three one-electron reductions with formal potentials of -1.13, -1.27 and -1.94 V which are largely ligand based. The electrocatalytic reduction of carbon dioxide is observed as an enhancement of the current at the ligand based process at -1.13 V (by about 100%). An even greater enhancement (by about 500%) is observed at the ligand based process at -1.27 V. The value of -1.13 V represents a diminution of about 0.8 V in the potential for carbon dioxide reduction, which is equivalent to that observed for the analogous nickel complex.

The complexes were also tested for catalytic activity in the reduction of oxygen. The complexes were isolated as chloride salts and dissolved in pH 4.5–12 aqueous buffer solutions. For all the cases tested, no significant catalytic effect for the reduction for oxygen was observed.

As an example, Fig. 2 presents the cyclic voltammograms for $Ni(tpy)_2(Cl)_2$ in a pH 8.4 aqueous $Na_2B_4O_7$/HCl buffer solution under nitrogen and oxygen atmospheres. Under nitrogen (solid line), the complex exhibits two one-electron reductions at -0.79 and -1.00 V. In an oxygen atmosphere, a new wave is observed close to -0.5 V due to the two-electron reduction of oxygen to peroxide. This wave appears unaltered from that observed in the absence of $Ni(tpy)_2(Cl)_2$ (but for an O_2 saturated solution) and therefore, in this case, no catalytic activity is observed. Similar results were obtained for the other complexes.

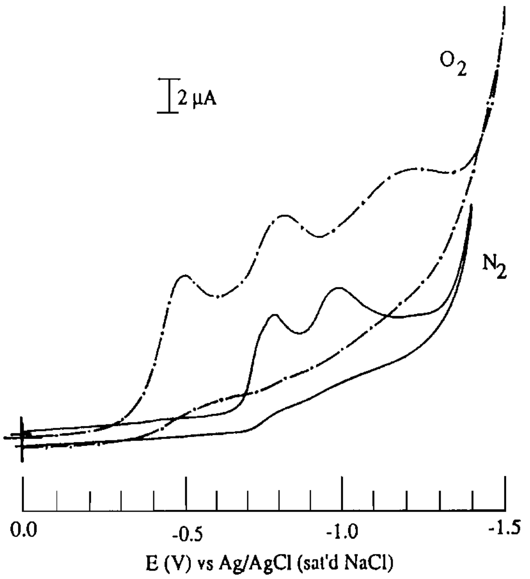

Fig. 2. Cyclic voltammogram at 10 mV s^{-1} of $Ni(tpy)_2Cl_2$ in a pH 8.4 aqueous $Na_2B_4O_7$/HCl buffer solution saturated with nitrogen and oxygen, respectively.

3.2. Electropolymerized films of $[M(v\text{-}tpy)_2]^{2+}(PF_6)_2$ as catalysts

In this section, we discuss the behavior of complexes that contain the electropolymerizable ligand vinyl-terpyridine. The complexes $Ni(v\text{-}tpy)_2(PF_6)_2$ and $Fe(v\text{-}tpy)_2(PF_6)_2$ will be discussed as well as the previously reported $Co(v\text{-}tpy)_2(PF_6)_2$ [14], which is included here for comparison purposes. Electrochemical data for these complexes, as well as the reduction potential for carbon dioxide at electrodes modified with polymeric films of these complexes, are presented in Table 1. In addition to describing the catalytic activity of these complexes for the reduction of carbon dioxide, their catalytic activity towards the two- and four-electron reduction of oxygen will be discussed as well.

In general, the complexes $M(v\text{-}tpy)_2(PF_6)_2$, where M = Ni, Fe and Co, undergo electroreductively initiated polymerization which gives rise to electrodes modified with an electroactive polymeric film of the complex [14]. The polymeric films exhibit redox processes at approximately the same potentials at those observed in solutions of the complexes. At slow sweep rates, these redox processes exhibited shapes characteristic of surface-bound species with the waves being symmetrical across the potential and current axes and with small ΔE_p values. However at faster sweep rates (>200 mV s^{-1}) the waves take on a 'diffusional' shape and ΔE_p increases significantly. Plots of peak current versus sweep rate were linear at slow sweep rates, as anticipated for surface-bound species, but there was some curvature for sweep rates beyond 200 mV s^{-1}, consistent with the previous discussion.

Surface coverages of the electropolymerized films were determined by integration of the area under the redox waves. For these complexes, a coverage of one monolayer corresponds to approximately 1×10^{-10} mol cm^{-2} of monomer units.

The electropolymerized films were found to be quite robust and resistant to continuous washings with water, acetone, acetonitrile and DMF. In addition, they were also quite stable to potential cycling with less than 10% loss after 6 h of continuous cycling.

The behavior of electropolymerized films of Ni(v-tpy)$_2$(PF$_6$)$_2$ and Fe(v-tpy)$_2$(PF$_6$)$_2$ are discussed below in some detail and compared to the results for the analogous Co(v-tpy)$_2$(PF$_6$)$_2$ complex [14].

3.2.1. *Ni(v-tpy)$_2$(PF$_6$)$_2$*

An acetonitrile solution of the complex Ni(v-tpy)$_2$(PF$_6$)$_2$ exhibits two metal based processes at +1.62 and −1.25 V. The one-electron oxidation observed at +1.62 V corresponds to an Ni(III/II) process, whereas the one-electron reduction observed at −1.25 V is ascribed to an Ni(II/I) process. An additional, one electron wave observed at −1.45 V is ascribed to a ligand localized reduction. When the potential of a platinum electrode in contact with a fresh solution of Ni(v-tpy)$_2$(PF$_6$)$_2$ in acetonitrile/0.1 M TBAP is scanned between 0.0 and −1.40 V (inset to Fig. 3) no electropolymerization is observed. This finding is in agreement with the assignment of this wave as an Ni(II/I) process since no electropolymerization is expected from a metal based reduction. If the potential is scanned more negatively than the ligand localized reduction at −1.45 V, by scanning from 0.0 to −1.70 V, electropolymerization readily occurs as can be observed in the main panel of Fig. 3. Upon polymerization in acetonitrile, new waves appear in the potential region between 0.0 and −0.40 V and −0.90 and −1.10 V, presumably due to partial dissociation of the ligand and coordination of the metal centers by solvent molecules as we have reported earlier for the analogous cobalt complex [14]. When the complex is electropolymerized in a slightly less coordinating solvent such as DMF, no new waves are observed. Furthermore, when an electrode which has been modified with a film of poly-Ni(v-tpy)$_2$(PF$_6$)$_2$ in acetonitrile is placed in a DMF solution containing only supporting electrolyte, these new waves disappear, once again pointing to the solvent dependence of these processes. In addition, these additional waves are characteristic of electropolymerized films since they are not observed in solutions of Ni(tpy)$_2$(PF$_6$)$_2$.

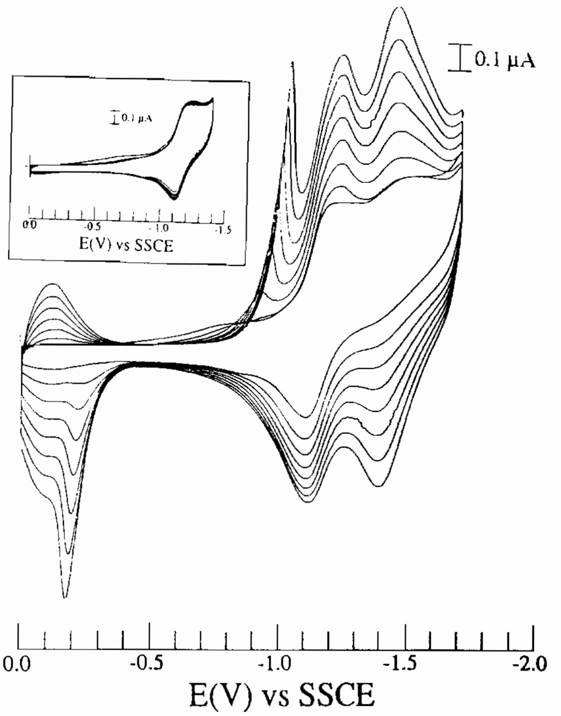

Fig. 3. Cyclic voltammogram for a platinum electrode in contact with a solution of Ni(v-tpy)$_2$(PF$_6$)$_2$ in 0.1 M TBAP/ACN scanned at 100 mV s^{-1} between 0.0 and −1.7 V. Inset: cyclic voltammogram at a freshly polished platinum electrode in contact with a solution of Ni(v-tpy)$_2$(PF$_6$)$_2$ in 0.1 M TBAP/ACN scanned at 100 mV s^{-1} between 0.0 and −1.40 V.

Electropolymerized films of this material were found to be effective for the electrocatalytic reduction of carbon dioxide exhibiting a large enhancement in the current (compared to the current under an N$_2$ atmosphere) at a potential of −1.22 V, which represents a very strong effect (a diminution of about 0.80 V in the overpotential) relative to the reduction of carbon dioxide at a bare electrode in the same medium.

The kinetics of this process were investigated via rotated disk electrode voltammetry experiments. Plots of i_{lim} versus $\omega^{1/2}$ (Levich plots) were linear at low rotation rates implying that under these conditions, the reaction is under mass transport control. However, at fast rates of rotation, the limiting currents leveled off, suggesting a kinetic limitation. Under these conditions, the Koutecky–Levich [27] equation can be used to determine the rate constant for the process. The Koutecky–Levich equation can be formulated as follows

$$1/i_{\text{lim}} = 1/(nFAk\Gamma C_b) + 1/(0.62nFAv^{-1/6}D^{2/3}\omega^{1/2}C_b) \qquad (6)$$

where C_b is the bulk concentration of the reactant in solution (in this case the solution concentration of CO$_2$ at saturation was estimated to be 215 mM [28,29]), Γ is the total surface coverage, v is the kinematic viscosity, ω is the rate of rotation, k is the rate constant with all other symbols having their conventional meaning. From Eq. (6) it is apparent that the value of k can be determined from the intercept of a plot of $1/i_{\text{lim}}$ versus $1/\omega^{1/2}$ (or a so-called Koutecky–Levich plot).

Fig. 4 presents a Koutecky–Levich plot ($1/i_{\text{lim}}$ versus $1/\omega^{1/2}$) for the electrocatalytic reduction of CO$_2$ (at −1.22 V) at an electrode modified with an electro-

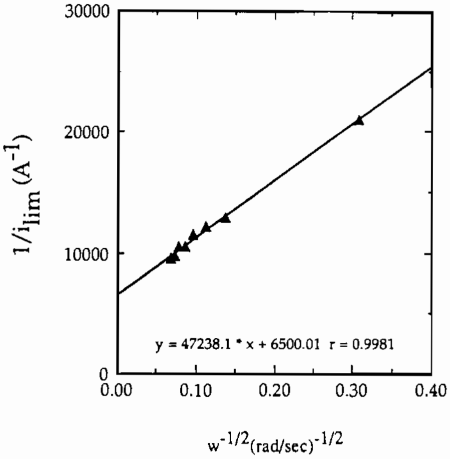

Fig. 4. Koutecky–Levich plot for the reduction of carbon dioxide at a glassy carbon electrode modified with an electropolymerized film of Ni(v-tpy)$_2$(PF$_6$)$_2$ at a coverage of 5.9 equivalent monolayers.

polymerized film of [Ni(v-tpy)$_2$]$^{2+}$ at a coverage of 5.9 equivalent monolayers (5.9×10^{-10} mol cm^{-2}). From the intercept of the plot, we obtain a value of about 40 M^{-1} s^{-1} for the second-order rate constant for the electrocatalytic process (ostensibly between the reduced complex and CO$_2$) in DMF/0.1 M TBAP solution. Although the rate constant has a rather modest value, the diminution in the activation energy for the reduction of carbon dioxide of about 0.80 V is quite dramatic.

Electropolymerized films of Ni(v-tpy)$_2$(PF$_6$)$_2$ were also found to catalyze both the two- and the four-electron reduction of oxygen. As previously described, in homogeneous solution, Ni(tpy)$_2$(PF$_6$)$_2$ did not show any catalytic effect on the two- nor the four-electron reduction of oxygen. When using electrodes modified with electropolymerized films of Ni(v-tpy)$_2$(PF$_6$)$_2$, however, not only is the two-electron reduction of oxygen observed at lower potentials, but the four-electron reduction of oxygen to water is observed as well.

As shown in Fig. 5, at electrodes modified with electropolymerized films of Ni(v-tpy)$_2$(PF$_6$)$_2$, the potential for the two-electron reduction of oxygen to hydrogen peroxide is shifted anodically by 100 mV, clearly indicating a lowering of the activation energy for that reaction. The voltammogram also shows a second reduction process at -1.00 V corresponding to the direct four-electron reduction of oxygen to water. It was also found that the polymer coverage greatly influenced which reduction process dominated. At low coverages, the two-electron reduction to peroxide was dominant whereas at higher coverages, the overall four-electron reduction of oxygen to water dominated (vide infra).

Rotated-ring–disk electrode experiments were carried out to study both reactions. Fig. 6 shows a rotated-ring–disk voltammogram in a pH 8.4 aqueous Na$_2$B$_4$O$_7$/HCl buffer solution saturated with oxygen for a glassy carbon disk electrode modified with an electropolymerized film of [Ni(v-tpy)$_2$]$^{2+}$ (at a coverage of 8.39×10^{-9} mol cm^{-2}) and a platinum ring electrode rotated at 1000 rpm. The solid line represents the current at the polymer-modified glassy carbon disk as it is scanned from 0.0 to -1.5 V whereas the dashed line represents the current measured at the platinum ring, which is held at $+0.80$ V. As the electrode rotates, the hydrodynamic flow carries solution from the bulk towards the disk and then radially outward towards the ring. Hence, by holding the potential of the ring at $+0.80$ V, any peroxide that is produced at the disk will be detected at the ring. At this potential, water produced at the disk will not be detected at the ring, and, therefore, the current at the ring is a direct measure of the peroxide produced.

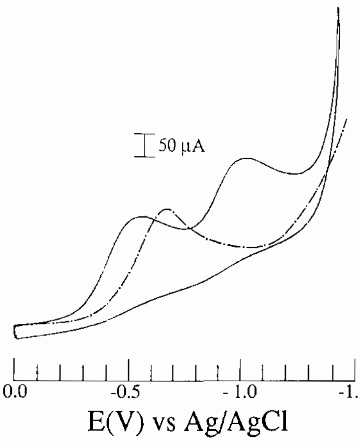

Fig. 5. Cyclic voltammograms at 10 mV s^{-1} for a bare glassy carbon electrode (— · —) and for a glassy carbon electrode modified with an electropolymerized film of Ni(v-tpy)$_2$(PF$_6$)$_2$ (——) both in a pH 8.4 aqueous Na$_2$B$_4$O$_7$/HCl buffer solution saturated with oxygen.

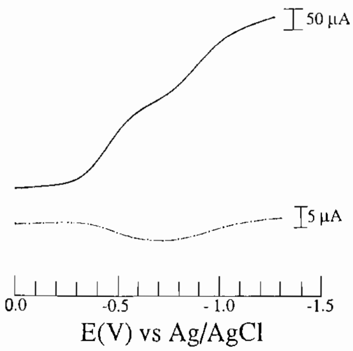

Fig. 6. Rotated-ring–disk electrode voltammograms at 10 mV s^{-1} for a glassy carbon disk (——) modified with an electropolymerized film of Ni(v-tpy)$_2$(PF$_6$)$_2$ at a coverage of 8.39×10^{-9} mol cm^{-2} rotated at 1000 rpm and scanned between 0.0 and -1.5 V and a platinum ring (— · —) held at -0.80 V in a pH 8.4 aqueous Na$_2$B$_4$O$_7$/HCl buffer solution saturated with oxygen.

As shown in Fig. 6, as the potential of the disk is scanned from 0.0 to -1.50 V, the currents at both the disk and the ring increase, implying the production of peroxide at the modified disk electrode. When the potential of the disk reaches −0.75 V, the current at the disk increases again, indicating that an additional redox process is occurring. Simultaneously, the current at the ring decreases and approaches the background value indicating that no peroxide is being generated. Given the decrease in current at the ring, the second redox process is ascribed to the direct four-electron reduction of oxygen to water.

The second-order rate constants for both reactions were determined from Koutecky–Levich plots for various coverages between 16.5 and 99.0 equivalent monolayers for oxygen-saturated pH 8.4 aqueous $Na_2B_4O_7$/HCl buffer solutions. Fig. 7 shows the Koutecky–Levich plots for the two- and four-electron reduction of oxygen at a glassy carbon electrode modified with an electropolymerized film of $Ni(v\text{-}tpy)_2(PF_6)_2$ at a coverage of 8.4×10^{-9} mol cm^{-2}. Table 2 presents the second-order rate constants for both processes, as a function of surface coverage, as determined from the intercepts of the Koutecky–Levich plots. It should be noted that the rate constants for both the two-electron reduction to peroxide as well as the four-electron reduction to water are significantly larger than for the reduction of carbon dioxide. However, the diminution of the activation energy is also significantly smaller for the reduction of O_2 relative to CO_2. Thus, the observed behavior would appear to be a compromise between the diminution of the activation energy on the one hand and the kinetics of the process, on the other.

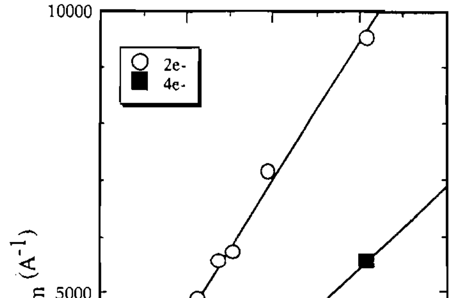

Fig. 7. Koutecky–Levich plots ($1/i_{lim}$ vs. $\omega^{-1/2}$) for the two- and four-electron reduction of oxygen at a glassy carbon electrode modified with 83.9 equivalent monolayers of poly-$Ni(v\text{-}tpy)_2^{2+}$ in pH 8.4 aqueous $Na_2B_4O_7$/HCl buffer solution.

TABLE 2

Second-order rate constants for the two- an four-electron reduction of oxygen in pH 8.4 aqueous $Na_2B_4O_7$/HCl buffer solution at glassy carbon electrodes modified with electropolymerized films of $Ni(v\text{-}tpy)_2(PF_6)_2$ at different coverages

Surface coverage ($\times10^9$ mol cm^{-2})	$[O_2]$ (mol dm^{-3})	$k(2e^-)$ (M^{-1} s^{-1})	$k(4e^-)$ (M^{-1} s^{-1})
8.39	1.4×10^3	7.6×10^2	7.3×10^2
1.65	1.4×10^3	7.7×10^3	6.3×10^3
9.90	1.4×10^3	4.4×10^2	4.5×10^2
2.97	1.4×10^3	2.6×10^3	1.8×10^3
2.54	1.4×10^3	4.9×10^3	4.5×10^3
5.38	1.4×10^3	6.9×10^2	6.7×10^2

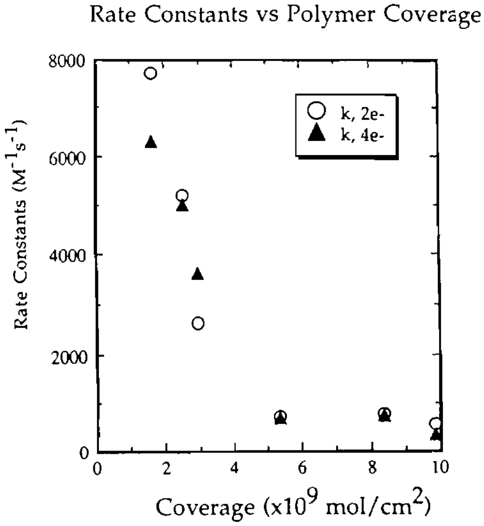

Fig. 8. Plot of second-order rate constants for the two- and four-electron reduction of oxygen in pH 8.4 aqueous $Na_2B_4O_7$/HCl buffer solution catalyzed by electropolymerized films of $Ni(v\text{-}tpy)_2(PF_6)_2$ vs. surface coverage of polymer film.

Fig. 8 presents a plot of rate constants versus polymer coverage for the two- and the four-electron reduction of oxygen to peroxide and water, respectively. There are two general trends that can be identified. First of all, it is evident that at higher coverages, the rate constants for both processes are lower than at lower coverages. This is especially true for coverages above 3×10^{-9} mol cm^{-2} where there is a significant drop. This effect is attributed to limitations due to transport of reactants and/or counterions within the polymeric structure. In addition, it is also clear that for coverages between about 1.5 to 3×10^{-9} mol cm^{-2}, where the decrease in the rate constants with coverage is less dramatic, there is a reversal in terms of the magnitude of the rate constants for the two- and four-electron reduction of oxygen to peroxide and water. That is, at the lower coverages ($\sim1.5\times10^{-9}$ mol cm^{-2}) the two-electron reduction to peroxide predominates. At intermediate coverages ($\sim2.5\times10^{-9}$ mol cm^{-2}) the rates are virtually the same and at higher coverages

(~3×10^{-9} mol cm^{-2}) the rate constant for the four-electron reduction of oxygen to water predominates. This behavior again suggests some cooperativity effects as have been previously demonstrated for the analogous cobalt complex [14].

3.2.2. $Fe(v\text{-}tpy)_2(PF_6)_2$

In acetonitrile solution, this complex exhibits two one-electron reductions at formal potentials of −1.12 and −1.28 V (Fig. 9(A)), which are both ascribed to ligand based processes. At positive potentials, there is a metal-localized Fe(III/II) process at +1.04 V (not shown in Fig. 9). During the electropolymerization process in acetonitrile/0.10 M TBAP solution, a new reversible wave (not present for the complex in solution) grows in with a formal potential of −0.10 V. This behavior is analogous to that mentioned earlier for electropolymerized films of $Ni(v\text{-}tpy)_2(PF_6)_2$. As in the case of $Ni(v\text{-}tpy)_2(PF_6)_2$, these waves were not observed when the voltammetric experiments were performed in DMF solution (Fig. 9(B)), and, therefore, the new waves observed in acetonitrile have been identified as partial displacement of the ligand and coordination by acetonitrile. We have previously reported on similar behavior for electropolymerized films of $Co(v\text{-}tpy)_2(PF_6)_2$ [14].

Electropolymerized films of $Fe(v\text{-}tpy)_2(PF_6)_2$ are effective in the electrocatalytic reduction of carbon dioxide as shown on Fig. 10. The solid line represents the voltammetric response at a glassy carbon electrode modified with an electropolymerized film of poly-$Fe(v\text{-}tpy)_2(PF_6)_2$ at a coverage of 7.23×10^{-9} mol cm^{-2}, which corresponds to approximately 72.3 equivalent monolayers, in 0.10 M TBAP/DMF solution saturated with nitrogen. The dashed line represents the voltammetric response in 0.10 M TBAP/DMF solution saturated with carbon dioxide. Under a carbon dioxide atmosphere, the current for the broad, two-electron wave is greatly enhanced and, in addition, there is no return wave, which is consistent with a catalytic process. The onset of electrocatalytic activity in this case was observed at about −1.0 V, which again represents a dramatic diminution in the activation energy by about one volt relative to the direct reduction of CO_2 at a glassy carbon electrode in DMF/0.10 M TBAP.

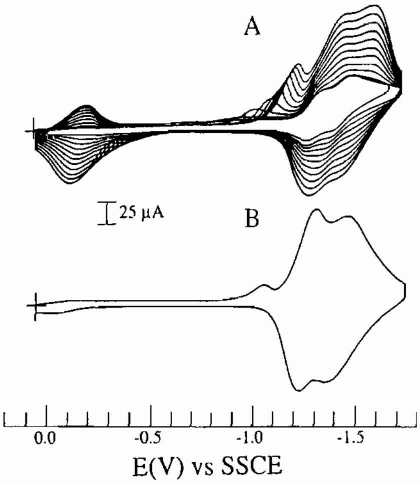

Fig. 9. (A) Cyclic voltammogram at a freshly polished platinum electrode in contact with a solution of $Fe(v\text{-}tpy)_2(PF_6)_2$ in 0.10 M TBAP/ACN showing 11 scans of electropolymerization at 100 mV s^{-1}. (B) Cyclic voltammogram of a platinum electrode modified with an electropolymerized film of $Fe(v\text{-}tpy)_2(PF_6)_2$ in 0.1 M TBAP/DMF at 100 mV s^{-1}.

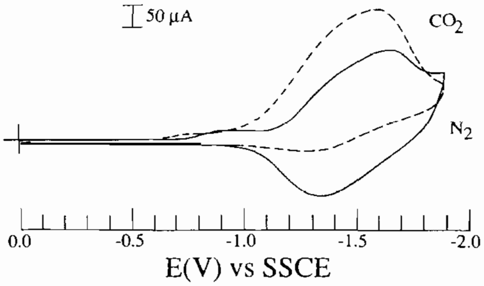

Fig. 10. Cyclic voltammogram at 100 mV s^{-1} for a platinum electrode modified with a electropolymerized film of $Fe(v\text{-}tpy)_2(PF_6)_2$ in 0.1 M TBAP/DMF under nitrogen and carbon dioxide atmospheres, respectively.

It is worth comparing the behavior of the various materials studied in terms of whether the material is in solution or immobilized on the electrode surface as well as the effect of the nature of the metal center.

In the first case we notice that for all the complexes studied, the electropolymerized films exhibited much higher catalytic activity than the corresponding materials in homogeneous solution. We believe this to be due to the fact that as a polymerized film the effective (volume) concentration of the metal complexes can achieve values in the vicinity of 0.5 M which are simply not accessible in solution. Under these conditions, the distance between metal centers is small enough that cooperativity effects can play a major role. This is especially evident in studies of the electrocatalytic reduction of oxygen where we find that the dominant pathway (i.e. two-electron reduction to peroxide or four-electron reduction to water) is strongly dependent on coverage. However, the fact that at higher coverage values the magnitude of the rate constants decreases, could imply that not all of the electrodeposited material is accessible. Thus, one must reach a compromise between these two competing processes.

In terms of the metal center, we find that the electrocatalytic behavior is dependent on the nature of the metal center. The number of electrons transferred (number of redox process), the potentials at which they occur as well as the nature of the redox processes, that is whether they are metal or ligand localized, are dependent on the identity of the metal center and thus have a significant effect on the electrocatalytic activity.

In general we find that cobalt complexes exhibit the highest activity followed by iron and nickel. We believe that the superior activity of the cobalt complexes might be due, in part, to the possibility of having the complexes act (formally) as two-electron donors through Co(III/I) couples. Such a possibility is not available for the iron nor the nickel complexes and we believe that this, in part, is responsible for the higher activity of the cobalt complexes. We are continuing further studies of these and related materials in terms of their potential electrocatalytic activity.

4. Conclusions

Transition metal complexes of Fe, Ni and Co incorporating terpyridine ligands are effective electrocatalysts for the reduction of carbon dioxide. All the complexes prepared exhibited some degree of electrocatalytic activity. The metal center plays a significant role in determining the electrocatalytic activity of the complex.

Electropolymerized films of v-tpy complexes of Fe, Ni and Co were also found to be effective catalysts for both the reduction of carbon dioxide and for the two- and four-electron reduction of oxygen. In general, a higher catalytic activity was found for the electropolymerized films relative to the complexes in homogeneous solution. In the case of the reduction of oxygen, the predominant reaction pathway was dependent on the surface coverage.

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