

## Electrocatalytic Reduction of Thionyl Chloride by Schiff Base Metal(II) Complexes (1)

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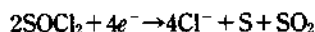
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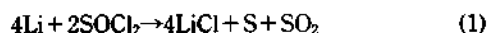
Catalytic effects of various Schiff base metal(II) complexes on the reduction of thionyl chloride at glassy carbon electrode are evaluated by determining the kinetic parameters from cyclic voltammetry technique. The charge transfer process is affected strongly by the concentration of catalysts during the reduction of thionyl chloride. The catalytic effects are shown by both a shift of the reduction potential for thionyl chloride toward more positive direction and an increase in peak current. The diffusion coefficient value,  $D_0$ , of the  $8.17 \times 10^{-9}$  cm<sup>2</sup>/s was observed at the bare glassy carbon electrode, whereas larger values ( $0.9\text{--}1.09 \times 10^{-8}$  cm<sup>2</sup>/s) were observed at the catalyst supported glassy carbon electrode. Significant improvements in the cell performance have been noted in terms of both exchange rate constants and current densities at glassy carbon electrode.

### Introduction

The electrochemical reduction of thionyl chloride has been studied extensively due to its importance in primary batteries.<sup>1-24</sup> In a lithium-thionyl chloride battery, neat thionyl chloride serves both as a solvent and as a catholyte. The common electrolyte used for primary active cells is lithium aluminum chloride (LiAlCl<sub>4</sub>) in SOCl<sub>2</sub> at fairly high concentration. The electrode kinetics of the cathode discharge reaction is rather poor due to the formation of passive LiCl films at the cathode as a result of the following reaction:



or



On the other hand, the LiCl passive film protects the underlying Li anode from undergoing spontaneous reactions with thionyl chloride, the film is also the source of the voltage delay owing to its overly passive nature. Thus many investigators tried to get around this high passivity problem. One approach to the enhancement of cell performance can be the addition of catalyst molecules, which makes the rate of electron transfer faster. It has been shown by Doddapaneni<sup>19-23</sup> that adding a small amount of metal phthalocyanines improves cell performance by changing both thermodynamic and kinetic parameters for the thionyl chloride reduction. Bernstein and Lever<sup>25</sup> described the reduction of thionyl chloride with phthalocyanine molecule in 1,2-dichlorobenzene.

In this paper, we report the effect of several Schiff base metal(II) complexes on the catalytic reduction of thionyl chloride by evaluating electrokinetic parameters involved. To our knowledge, this is the first effort to evaluate the effect of these catalyst molecules quantitatively.

### Experimental

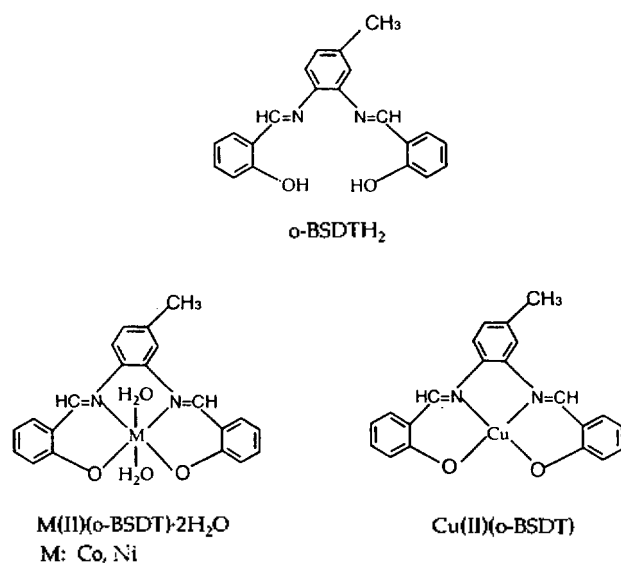
The originals salicylaldehyde (Merck), 3,4-diaminotoluene (Aldrich), 2,5-diaminotoluene hydrochloride (Aldrich), Na<sub>2</sub>CO<sub>3</sub>,

**Table 1.** Elemental Analysis Data of the Ligands and Complexes

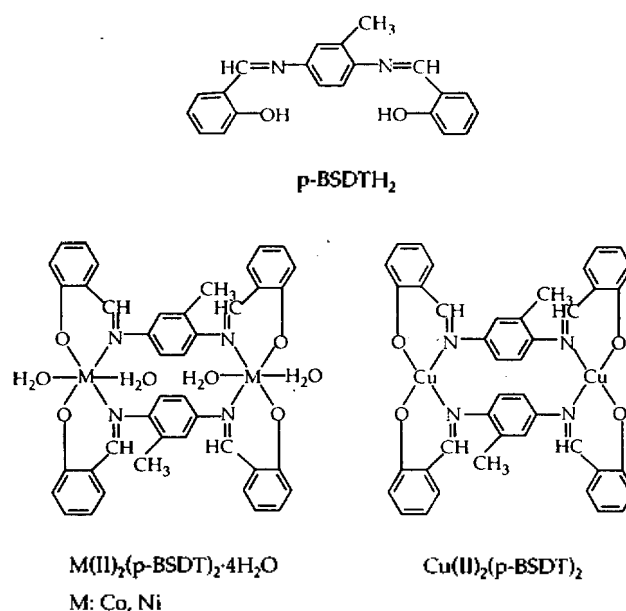
Ligands & complexes	Metal (%)	C (%)	H (%)	N (%)	
<i>o</i> -BSDTH <sub>2</sub>	Cal.	—	76.34	5.49	8.48
	Foun.	—	76.38	5.52	8.50
Co(II)( <i>o</i> -BSDT)(H <sub>2</sub> O) <sub>2</sub>	Cal.	13.86	59.30	4.74	6.59
	Foun.	13.84	59.32	4.63	6.71
Ni(II)( <i>o</i> -BSDT)(H <sub>2</sub> O) <sub>2</sub>	Cal.	13.80	59.33	4.74	6.59
	Foun.	13.98	59.93	4.53	6.57
Cu(II)( <i>o</i> -BSDT)	Cal.	16.13	64.03	4.09	7.11
	Foun.	16.36	64.17	3.99	7.23
<i>p</i> -BSDTH <sub>2</sub>	Cal.	—	76.34	5.49	8.48
	Foun.	—	76.33	5.49	8.44
Co(II) <sub>2</sub> ( <i>p</i> -BSDT) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	Cal.	13.86	59.30	4.03	6.59
	Foun.	13.90	60.42	4.75	6.68
Ni(II) <sub>2</sub> ( <i>p</i> -BSDT) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	Cal.	13.80	59.33	4.03	6.59
	Foun.	14.01	60.51	4.72	6.69
Cu(II) <sub>2</sub> ( <i>p</i> -BSDT) <sub>2</sub>	Cal.	16.13	64.03	4.09	7.11
	Foun.	16.31	64.50	3.98	7.11

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, NaOH, and ethanol were used. The elemental analysis (carbon, hydrogen, and nitrogen) was performed by a Yanaco-CHN coder MT-3 analyzer, and the metal content was determined by a Perkin-Elmer model 603 atomic absorption spectrophotometer. The results of elemental analysis of the Schiff base ligand (*o*-BSDTH<sub>2</sub>, *p*-BSDTH<sub>2</sub>) and their complexes (M(II)(*o*-BSDT), M(II)<sub>2</sub>(*p*-BSDT)<sub>2</sub>) are listed in Table 1. Infrared and UV-vis spectra were recorded by Shimadzu IR-430 infrared and Hitachi-557 UV-vis spectrophotometers. Thermogravimetric analysis was carried out by a Perkin-Elmer model 2 Thermogravimetric Analyzer.

A quadridentate Schiff base ligand, 3,4-bis(salicylidene diimine) toluene, [*o*-BSDTH<sub>2</sub>] and 2,5-bis(salicylidene diimine) toluene, [*p*-BSDTH<sub>2</sub>] were prepared by the following me-



Scheme 1.



Scheme 2.

thod. A 0.1 mole 3,4-diaminotoluene solution in ethanol was slowly added to the same volume of 0.1 mole salicylaldehyde in ethanol under the nitrogen atmosphere. When the mixed solution was slowly stirred, a yellow *o*-BSDTH<sub>2</sub> precipitate was obtained.

A 0.1 mole 2,5-diaminotoluene hydrochloride solution in ethanol was slowly added to the same volume of 0.1 mole salicylaldehyde in ethanol under the nitrogen atmosphere. When the mixed solution was slowly stirred, an orange *p*-BSDTH<sub>2</sub> precipitate was obtained. The precipitates were recrystallized in ethanol and dried under the reduced pressure at 80 °C.

The complexes,  $M(II)(o\text{-BSDT})$  ( $M = Co, Ni, Cu$ ), were prepared by the slowly addition of 0.1 mole *o*-BSDTH<sub>2</sub> in ethanol to the same volume of 0.1 mole  $M(II)(NO_3)_2 \cdot (H_2O)_6$  in ethanol, while stirred under the nitrogen atmosphere.

The complexes,  $M(II)_2(p\text{-BSDT})_2$ , were also prepared by the addition of 0.1 mole *p*-BSDTH<sub>2</sub> in ethanol to the same volume of 0.1 mole  $M(II)(NO_3)_2 \cdot (H_2O)_6$  in water, while stirred under the nitrogen atmosphere. The precipitates obtained were then recrystallized from ethanol and dried at 80 °C under the reduced pressure.

Single electrochemical compartment cell housed glassy carbon working (geometric area, 0.071 cm<sup>2</sup>), a platinum wire counter, and a lithium wire reference electrodes. Glassy carbon electrode was polished to a mirror finish with 1 μm alumina powder, subsequently cleaned in an ultrasonic cleaning bath for the removal solid particles, and finally rinsed with a copious amount of doubly distilled deionized water before use. The original 1.53 M LiAlCl<sub>4</sub>/SOCl<sub>2</sub> electrolytic solution (LITHCO) was used. All experiments were conducted in a glove box under the Ar gas atmosphere. A Princeton Applied Research (PAR) 273 potentiostat/galvanostat was used for recording cyclic voltammograms, which was interfaced by 486 DX microcomputer through an IEEE-488 bus.

## Results and Discussion

The results of elemental analysis of the Schiff base ligand

and their complexes agree well with the predicted composition of the proposed complexes, as shown in Scheme 1 and 2.

The content of metal in the  $M(II)_2(p\text{-BSDT})_2$  complexes is also in excellent agreement with the proposed complexes of one base molecule with two metal(II) ions. All complexes are insoluble in water but soluble in SOCl<sub>2</sub> solvent. The thermogravimetric analysis results are shown in Table 2. Hydrate water molecules are driven away between 80–320 °C and the metal oxides are formed above 600 °C for the Co(II), Cu(II), and Ni(II) complexes.

Tables 3-1 and 3-2 show the infrared spectra data of the ligands and their  $M(II)$  complexes. The spectra show broad  $\nu(OH)$  bands of the Co(II) and Ni(II) complexes at 3400 cm<sup>-1</sup>, but does not shown these of Cu(II) complexes. The IR spectra data suggest that the Co(II) and Ni(II) complexes contain water molecules.<sup>26</sup> Perhaps  $\nu(OH)$  in the hydrate water may be in a fairly strongly hydrogen bonded state, which may weaken the OH stretching motion.

We can also see that  $\nu(C=N)$  bands in the complex are shifted to the lower energy regions, 1610–1600 cm<sup>-1</sup> in the corresponding free ligands.<sup>27</sup> The similar trends are shown in the case of  $\nu(C-O)$  and  $\nu(C-N)$  bands.

Two bands at 800–830 cm<sup>-1</sup> and 555–565 cm<sup>-1</sup>, assigned to  $M(II)-N$  and  $M(II)-O$ , are clearly seen in Tables 3-1 and 3-2. According to Ueno and Martell,<sup>28</sup> characteristic absorption bands for  $M(II)-N$  and  $M(II)-O$  bonds in complexes appear respectively in the spectral region of 650–850 cm<sup>-1</sup> and 400–600 cm<sup>-1</sup>.

The UV-vis spectra (not shown) of the Co(II) and Ni(II) complexes obtained in pyridine show a  $\pi-\pi^*$  ligand field absorption band at 400 nm and a  $d-\pi^*$  charge transfer band at 470 nm. These observations are consistent with the proposed structure. Figure 1 shows cyclic voltammograms recorded in a thionyl chloride solution containing (a) 0.00 (b) 0.35 (c) 0.52 (d) 0.76 (e) 0.83 mM Co(II)(*o*-BSDT). As shown in

**Table 2.** Thermogravimetric Analysis Data of the Ligands and Complexes

Ligands & complexes	T.G.A.	Residue (%)
<i>o</i> -BSDTH <sub>2</sub>	Temp. (°C)	80-111-360-670
	Weight loss (%)	0 30.40 69.60
Co(II)( <i>o</i> -BSDT)(H <sub>2</sub> O) <sub>2</sub>	Temp. (°C)	80-270-640
	Weight loss (%)	8.63 73.35
Ni(II)( <i>o</i> -BSDT)(H <sub>2</sub> O) <sub>2</sub>	Temp. (°C)	80-305-610
	Weight loss (%)	8.45 73.74
Cu(II)( <i>o</i> -BSDT)	Temp. (°C)	80-200-615
	Weight loss (%)	0 78.95
<i>p</i> -BSDTH <sub>2</sub>	Temp. (°C)	80-127-405-720
	Weight loss (%)	0 63.11 36.89
Co(II) <sub>2</sub> ( <i>p</i> -BSDT) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	Temp. (°C)	80-260-680
	Weight loss (%)	8.49 73.67
Ni(II) <sub>2</sub> ( <i>p</i> -BSDT) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	Temp. (°C)	80-320-676
	Weight loss (%)	8.77 73.22
Cu(II) <sub>2</sub> ( <i>p</i> -BSDT) <sub>2</sub>	Temp. (°C)	80-250-703
	Weight loss (%)	0 79.46

**Table 3-1.** IR spectra (cm<sup>-1</sup>) of *o*-BSDTH<sub>2</sub> and Its M(II) Complexes

<i>o</i> -BSDTH <sub>2</sub>	Co(II) complex	Ni(II) complex	Cu(II) complex	Assignment
3030 m	3400 s.b.	3430 s.b.		
2950 m	3030 m	3050 m	3030 m	v(O-H) hydrate
	2900 m	2930 m	2930 m	v(C-H)(aromatic)
1622 vs	1608 vs	1610 vs	1612 vs	v(CH <sub>3</sub> )
1600 s.sh	1600 s.sh	1582 s	1598 s	v(C=N)(Schiff base)
	1528 s	1525 s	1535 s	v(C=C)(phenyl ring)
1560 s	1500 m	1507 m.sh	1507 m.sh	
1540 m.sh	1245 m.sh	1245 w	1250 w	v(C=C)(phenyl ring)
	1140 m	1148 m	1152 s	v(C-O)
1268 s	1025 w	1020 w	1030 w	v(C-N)
1178 s	805 w	800 w	802 w	
1023 m				v(M(II)-N)
	750 s	750 m	762 s	δ(CH)(out of plane)
765 vs	555 w	565 w	555 w	v(M(II)-O)

m; middle, vs; very strong, s; strong, sh; shoulder, w; weak.

this figure, shapes of voltammogram are affected strongly by the concentration of catalysts. This is the same with all M(II) complexes studied, although the extent of effects is different.

In Figure 2 and 3, peak currents and peak potentials are plotted the functions of the catalysts concentration for Co(II) (*o*-BSDT) and Co(II)<sub>2</sub>(*p*-BSDT)<sub>2</sub> complexes at glassy carbon electrode. The magnitude of the reduction current appears to be a strong function of catalyst concentration in thionyl chloride solution. It is clear that some M(II)(*o*-BSDT) and M(II)<sub>2</sub>(*p*-BSDT)<sub>2</sub> show sizable catalytic activities for the reduction of thionyl chloride. This fact indicates that the first step for the catalytic activity of these compounds must be the adsorption of catalyst molecules on the electrode surface,

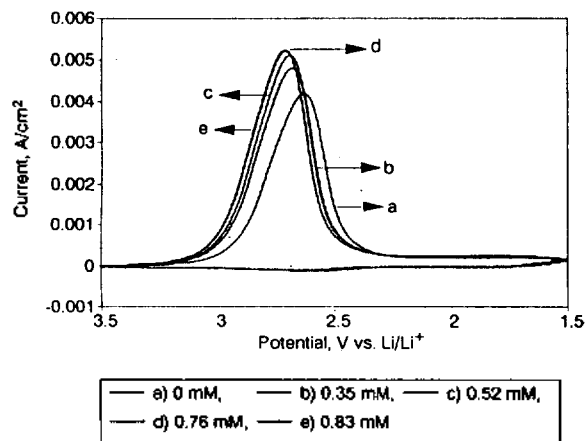
**Table 3-2.** IR Spectra (cm<sup>-1</sup>) of *p*-BSDTH<sub>2</sub> and Its M(II) Complexes

<i>p</i> -BSDTH <sub>2</sub>	Co(II) complex	Ni(II) complex	Cu(II) complex	Assignment
3030 m				
2850 m				
1620 vs	3350 m.b	3300 m.b		v(O-H) hydrate
	3000 m	3030 m	3000 m	v(C-H) (aromatic)
1565 s	2900 m	2870 m	2900 m	v(CH <sub>3</sub> )
	1597 vs	1600 vs	1600 vs	v(C=N)(schiff base)
	1570 s			v(C-C)(phenyl ring)
1495 m.sh	1520 s	1523 s	1525 s	
	1480 m	1480 s	1483 m	v(C=C)(phenyl ring)
1278 s	1280 m	1282 m	1286 m	v(C-O)
	1177 s	1177 s	1180 s	v(C-N)
1180 s	1105 w	1102 w	1100 w	
	825 w	826 w	828 w	v(M(II)-N)
1105 m	725 s	723 s	727 s	δ(CH)(out of plane)
	566 w	556 w	555 w	v(M(II)-O)
722 s				

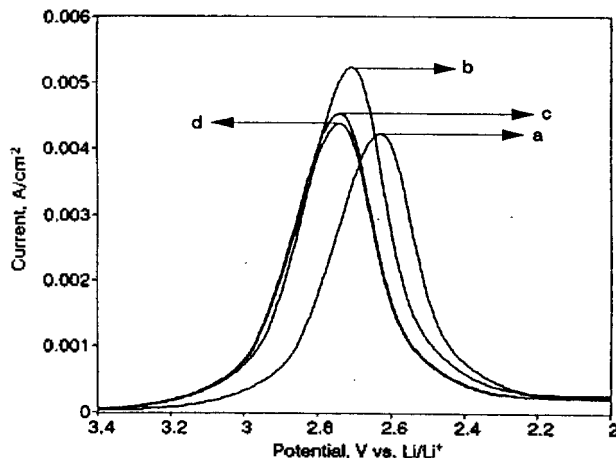
m; middle, vs; very strong, s; strong, sh; shoulder, w; weak.

followed by its own reduction at the electrode, which in turn reduces thionyl chloride.<sup>22</sup> There is an optimum concentration for each catalyst at around 0.7-0.8 mM. Figures 4 and 5 show voltammograms of catalytic effect in thionyl chloride solution containing M(II)(*o*-BSDT) and M(II)<sub>2</sub>(*p*-BSDT)<sub>2</sub> at glassy carbon electrode.

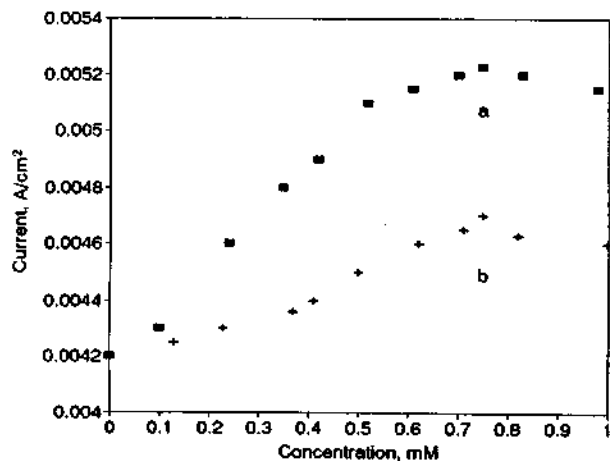
The catalytic effects are clearly seen by both the shift of the reduction potential for thionyl chloride toward positive direction and the increase of peak current. Peak currents and potentials observed for the reduction of thionyl chloride in the presence of several catalyst molecules are summarized in Table 4. The peak currents increase for most catalysts,



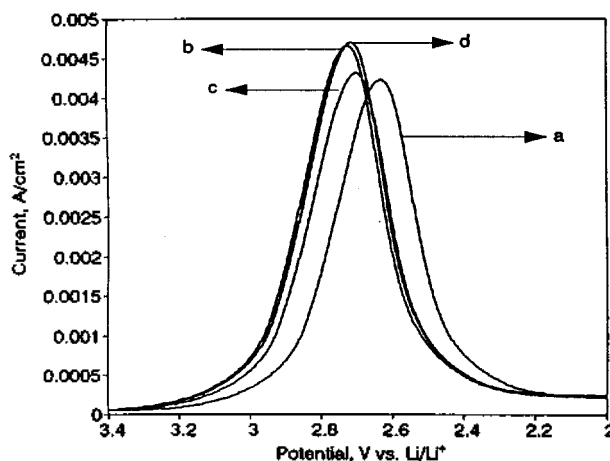
**Figure 1.** Cyclic voltammograms recorded at the glassy carbon electrode for the reduction of  $\text{SOCl}_2$  solution containing: a) 0, b) 0.35, c) 0.52, d) 0.76 and e) 0.83 mM  $\text{Co(II)(o-BSDT)}$ . Scan rate is 50 mV/s.



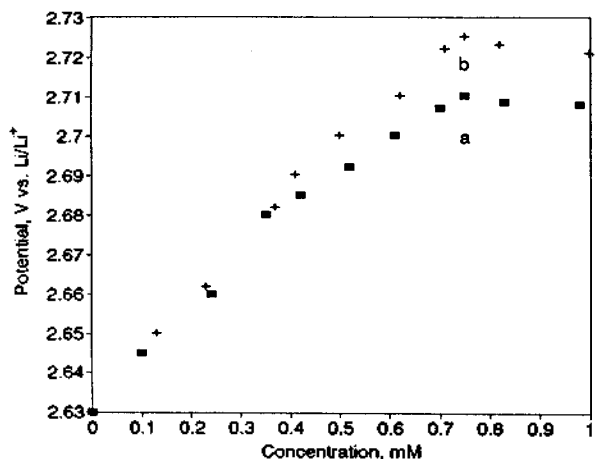
**Figure 4.** Voltammograms recorded at the glassy carbon electrode for the reduction of  $\text{SOCl}_2$  solution at optimum concentration containing: a) bare, b)  $\text{Co(II)(o-BSDT)}$ , c)  $\text{Ni(II)(o-BSDT)}$ , and d)  $\text{Cu(II)(o-BSDT)}$ . Scan rate is 50 mV/s.



**Figure 2.** Plots of the peak current vs. the concentration of catalysts for the reduction of  $\text{SOCl}_2$  at glassy carbon electrode: a)  $\text{Co(II)(o-BSDT)}$  and b)  $\text{Co(II)(p-BSDT)}_2$ .



**Figure 5.** Voltammograms recorded at the glassy carbon electrode for the reduction of  $\text{SOCl}_2$  solution at optimum concentration containing: a) bare, b)  $\text{Co(II)(p-BSDT)}_2$ , c)  $\text{Ni(II)(p-BSDT)}_2$ , and d)  $\text{Cu(II)(p-BSDT)}_2$ . Scan rate is 50 mV/s.



**Figure 3.** Plots of the peak potential vs. the concentration of catalysts for the reduction of  $\text{SOCl}_2$  at glassy carbon electrode: a)  $\text{Co(II)(o-BSDT)}$  and b)  $\text{Co(II)(p-BSDT)}_2$ .

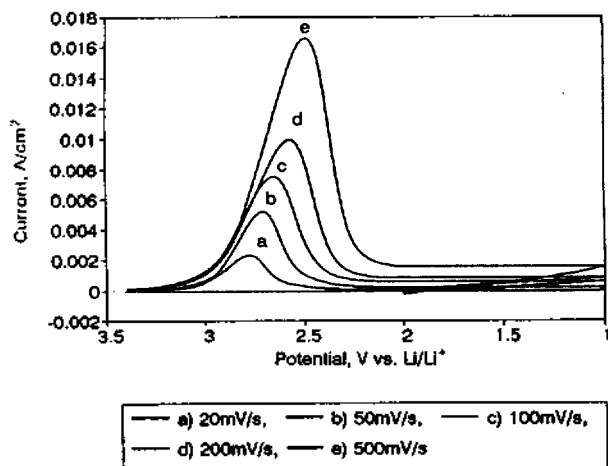
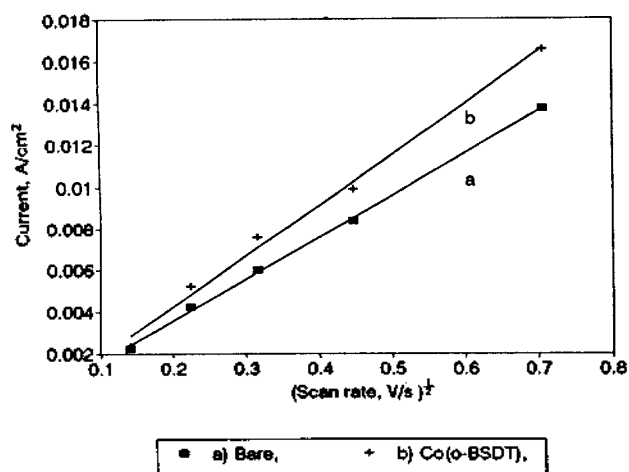
and potentials shift to positive direction. Thus these compounds show good catalytic activities at glassy carbon electrode. Relative catalytic effects are larger in thionyl chloride solution containing  $\text{M(II)(o-BSDT)}$  compared to  $\text{M(II)(p-BSDT)}_2$ .

Cyclic voltammetric experiments only at an "optimum" catalyst concentration are conducted to evaluate kinetic parameters after waiting for some time until voltammograms are developed to a well defined shape. Voltammograms were taken after the electrode is immersed in a freshly prepared catalyst solution. The data, although some scattered points were observed, were reproducible, depending on the status of electrode surface.

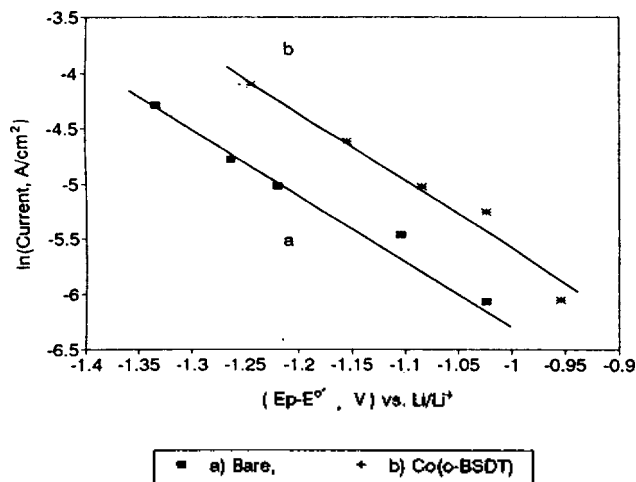
Figure 6 shows a series of cyclic voltammograms recorded at various scan rates ranging from 20-300 mV/sec in thionyl chloride solution containing 0.65 mM  $\text{Co(II)(o-BSDT)}$ . Figure 7 shows a plot of peak current vs.  $v^{1/2}$  ( $v$ : scan rate) from

**Table 4.** Peak Potentials and Peak Currents on the Reduction of  $\text{SOCl}_2$  at the Glassy Carbon Electrode

Catalysts	Concentration (mM)	Peak potential (V vs. $\text{Li/Li}^+$ )	Peak current ( $\text{A}/\text{cm}^2$ )
Bare	—	2.630	0.0042
$\text{Co(II)}(\text{o-BSDT})$	0.76	2.710	0.0052
$\text{Ni(II)}(\text{o-BSDT})$	0.73	2.740	0.0045
$\text{Cu(II)}(\text{o-BSDT})$	0.74	2.740	0.0044
$\text{Co(II)}_2(\text{p-BSDT})_2$	0.76	2.725	0.0047
$\text{Ni(II)}_2(\text{p-BSDT})_2$	0.79	2.700	0.0043
$\text{Cu(II)}_2(\text{p-BSDT})_2$	0.77	2.715	0.0047

**Figure 6.** Scan rate dependency of the voltammograms recorded at glassy carbon electrode for the reduction of  $\text{SOCl}_2$  solution containing 0.65 mM  $\text{Co(II)}(\text{o-BSDT})$ . Scan rate are a) 20, b) 50, c) 100, d) 200, and e) 300 mV/s.**Figure 7.** Plots of  $i_p$  vs.  $v^{1/2}$  at the glassy carbon electrode for the reduction of  $\text{SOCl}_2$  solution containing; a) 0 and b) 0.76 mM  $\text{Co(II)}(\text{o-BSDT})$ .

voltammetric results obtained at glassy carbon electrode under the "optimum" conditions. This plot shows linear relationship. The peak current from cyclic voltammetry in irre-

**Figure 8.** Plots of  $\ln(i_p)$  vs.  $(E_p - E^0)$  at the glassy carbon electrode for the reduction of  $\text{SOCl}_2$  solution containing; a) 0 and b) 0.76 mM  $\text{Co(II)}(\text{o-BSDT})$ .**Table 5.** Kinetic Parameters on the Reduction of  $\text{SOCl}_2$  at the Glassy Carbon Electrode

Catalysts	Concentration (mM)	$\alpha n_a$	$D_0$ ( $\text{cm}^2/\text{s}$ )	$k^0$ ( $\text{cm}/\text{s}$ )
Bare	—	0.1389	8.17E-09	2.25E-08
$\text{Co(II)}(\text{o-BSDT})$	0.76	0.1273	1.03E-08	3.42E-07
$\text{Ni(II)}(\text{o-BSDT})$	0.73	0.1740	1.03E-08	1.17E-07
$\text{Cu(II)}(\text{o-BSDT})$	0.74	0.1513	1.09E-08	2.66E-07
$\text{Co(II)}_2(\text{p-BSDT})_2$	0.76	0.1830	1.02E-08	2.30E-07
$\text{Ni(II)}_2(\text{p-BSDT})_2$	0.79	0.1868	8.62E-09	1.24E-07
$\text{Cu(II)}_2(\text{p-BSDT})_2$	0.77	0.1582	1.08E-08	1.86E-07

versible case is given as follows.<sup>29</sup>

$$i_p = (2.99 \times 10^5) n(\alpha n_a)^{1/2} A C_0^* D_0^{1/2} v^{1/2} \quad (2)$$

Examination of Eq. (2) reveals that the plot of  $i_p$  vs.  $v^{1/2}$  allows us to obtain the diffusion coefficient, provided  $\alpha$  and  $n_a$  are known. From the relationship of  $i_p$  with  $E_p$ <sup>29</sup>

$$i_p = 0.227 n F A C_0^* k^0 \exp[-\{(\alpha n_a F)/(RT)\}(E_p - E^0)] \quad (3)$$

A plot of  $\ln(i_p)$  vs.  $E_p - E^0$  should yield a straight line with a slope,  $\alpha n_a F/RT$ , and an intercept,  $\ln(0.227 n F A C_0^* k^0)$ , from which  $\alpha n_a$  and  $k^0$  values can be calculated, respectively. The  $\ln(i_p)$  vs.  $(E_p - E^0)$  plots are shown in Figure 8 for the reduction of  $\text{SOCl}_2$  at glassy carbon electrode in the presence of various catalysts. The  $\alpha n_a$  value obtained from this equation can be used to evaluate the diffusion coefficient according to Eq. (2). Kinetic parameters calculated from these plots in "optimum" catalyst concentrations are listed in Table 5. As can be seen Table 5, diffusion coefficient,  $D_0$ , and exchange rate constant,  $k^0$ , are determined to  $8.17 \times 10^{-9} \text{ cm}^2/\text{s}$  and  $2.25 \times 10^{-8} \text{ cm/s}$  at bare glassy carbon electrode. But diffusion coefficients are determined to  $0.9\text{--}1.09 \times 10^{-8} \text{ cm}^2/\text{s}$  and exchange rate constant are estimated to  $1.24\text{--}7.42 \times 10^{-7} \text{ cm/s}$  at catalyst supported glassy carbon electrode. Signifi-

cant improvements in cell performance are noted in terms of both exchange rate constants of up to 10 times and current densities of up to 124%.

Most enhancement originates from improvements in apparent diffusion coefficients and exchange rate constants in thionyl chloride solution containing catalysts. These result are in accordance with previous cell test results reported by Doddapaneni<sup>19-23</sup> on the reduction of  $\text{SOCl}_2$  solution containing metal phthalocyanine. Relative catalytic effects are larger in thionyl chloride solution containing schiff base metal complexes compared to cobalt phenylporphyrin reported by authors.<sup>24</sup> From our results, some quadridentate Schiff base  $\text{M(II)}(o\text{-BSDT})$  and  $\text{M(II)}_2(p\text{-BSDT})_2$  complexes show sizable catalytic activities for the reduction of thionyl chloride.

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