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Electrocatalytic Reduction of Molecular Oxygen by Mononuclear
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By

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Electrocatalytic Reduction of Molecular Oxygen by Mononuclear
and Binuclear Cobalt Phthalocyanir s

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Abstract

Investigations of the electrocatalytic activity of mononuclear and binuclear cobalt phthalocyanines for the reduction of molecular oxygen established that the latter compounds are more effective catalysts than the corresponding mononuclear species. A correlation between the half-bandwidths for the Q band of these species and their catalytic efficiency, expressed as a kinetically-limited current, suggests that the increase in activity may be attributed to electronic coupling between the phthalocyanine rings.

Introduction

If a fuel cell is to operate efficiently, a catalyst must be embedded in the cathode to accelerate the reduction of oxygen gas. This catalyst must be capable of withstanding the operating conditions of the fuel cell (strong acid or base, fairly high temperatures), for long periods of time, without loss of activity. Platinum is commonly used as a fuel cell catalyst, but is expensive representing some 10% of the total fuel cell cost. Catalysts which are more effective, and less expensive are needed, if fuel cell applications are to become viable.

Many mononuclear metal porphyrins act as electrocatalysts (1-21) but the work of Collman and Anson (22-28) and Chang (29-35) has revealed that certain binuclear porphyrins are much more effective. Similarly, mononuclear phthalocyanines of iron and cobalt are effective (36-50), but some ill-characterised 'dimeric' and polymeric phthalocyanines appear more effective (51-62). Savy (54-56) performed ESCA, ESR, Mössbauer and optical spectroscopic studies to establish correlations between the spectroscopic properties of polymeric and monomeric iron phthalocyanines and the electrocatalytic activity of these species towards oxygen reduction. We consider here a correlation between the optical spectra of a series of well-characterized mono- and binuclear cobalt phthalocyanines and

their electrocatalytic activity.

The binuclear porphyrins studied by Collman and Anson are too fragile for long-term use under fuel cell conditions and therefore our studies have been directed towards thermally more stable binuclear phthalocyanine compounds. We have recently reported (63-65) a series of binuclear phthalocyanine complexes of the general formula [M-tri(neopentoxy)phthalocyanine]$_2$(bridge) where the bridge may contain 1,2,4 or 5 atoms, and where M may be H$_2$, Cu or Co. The three neopentoxy groups are randomly distributed in the 4 or 5 positions of the three unbridged benzene rings, providing solubility in many organic solvents e.g. toluene, o-dichlorobenzene and dichloroethane, but generally not acetone and ethanol.

Of relevance to this presentation are the following species, with their abbreviations (the number in parentheses is the number of bridging atoms connecting the two phthalocyanine rings):

CoTNPc   2,9,16,23-tetraneopentoxyphthalocyanatocobalt(II). This is the mononuclear control molecule.

O(1)[CoTrNPc]$_2$ bis-2-(9,16,23-trineopentoxyphthalocyaninyl-cobalt(II))ether; two phthalocyanine rings linked by a single oxygen (ether) bridge.

C(2)[CoTrNPc]$_2$ 1,2-bis-2'-(9',16',23'-trineopentoxyphthalo-

cyaninylcobalt(II))ethane; two phthalocyanine rings linked by an ethane $-CH_2CH_2-$ bridge.

Cat(4)[CoTrNPc]$_2$ 1,2-bis-2'-(9',16',23'-trineopentoxyphthalo-cyaninoxycobalt(II))benzene; two phthalocyanine rings linked by a catechol $-O-C_6H_4-O-$ bridge.

EtMeO(5)[CoTrNPc]$_2$ 1,3-bis-2'-(9',16',23'-trineopentoxyphthalo-cyaninoxycobalt(II))-2-ethyl-2-methylpropane; two phthalo-cyanine rings attached linked by a $-OCH_2C(Et)(Me)CH_2O-$ bridge.

Earlier investigations of the metal-free analogues of these species (66) established properties of these compounds which are relevant to the observations reported here. These properties are:

i) In condensed phases (frozen solution glass, Nujol mull, etc.), these complexes may exhibit intermolecular aggregation. In dilute solution, <5 X 10^{-5} M, intermolecular aggregation is generally absent (67).

ii) Some binuclear phthalocyanines may close upon themselves ('clamshell' behaviour) to aggregate via cofacial intramolecular aggregation. Specifically, of the metal-free species, only Cat(4)[TrNPcH$_2$]$_2$ and EtMeO(5)[TrNPcH$_2$]$_2$ are capable of such intramolecular aggregation. Such species exist in a dynamic equilibrium with 'open' conformations.

iii) The electronic spectra of the metal-free species show evidence of the coupling of the transition moments on each

phthalocyanine ring (66). Thus direct through space coupling is observed in the cofacial conformations, giving rise to a blue shift in the Q and Soret absorptions. However, a blue shift is also observed in the other metal-free species, as a consequence of coupling through space (or through the bridge) in 'open', non-aggregated conformations.

Note that electronic coupling is more readily detected in the electronic spectra of binuclear phthalocyanine species, relative to comparable porphyrin species, because the visible region transition moments are much larger in the former case (68).

Experimental

The species Co(II)TNPc (64), EtMeO(5)[Co(II)TrNPc]$_2$ (64), C(2)[Co(II)TrNPc]$_2$ (65), Cat(4)[Co(II)TrNPc]$_2$ (65) and O(1)[Co(II)TrNPc]$_2$ (69) were prepared by literature routes. Aldrich Gold Label o-dichlorobenzene (DCB) was used without further purification and Fisher certified 1 N sodium hydroxide was diluted as required for the aqueous studies. Water was purified by double-distillation over $KMnO_4$ followed by passage through a Barnstead organic removal cartridge and two Barnstead mixed resin ultrapure cartridges. Stress-annealed pyrolytic graphite (SAPG) and ordinary pyrolytic graphite (OPG), obtained from Union Carbide, were used as electrode materials. The

graphite was mounted in Teflon to expose a circular area of 0.490 cm^2 for the SAPG electrode and 0.493 cm^2 for the OPG electrode. Before each experiment, the electrode surface was cleaned by successive polishings with 1.0 μm, 0.3 μm and 0.05 μm alumina (Linde) suspended in water on Metron polishing cloth. Argon gas (Linde) was purified by passage through heated copper filings, anhydrous CaSO$_4$ (Drierite), molecular sieves (BDH Type 3A), and glass wool. Oxygen gas (Linde) was purified by passage through anhydrous CaSO$_4$, NaOH pellets (AnalaR analytical grade), anhydrous CaSO$_4$, molecular sieves and glass wool. Tetrabutylammonium perchlorate (TBAP) (Eastman Kodak) was recrystallized from absolute ethanol and dried in a vacuum oven at 50°C for two days. Potential scans were performed with a Pine Instruments RD3 potentiostat and the rotation studies with a Pine Instruments PIR rotator. The cell for the adsorption experiments employed a medium frit to separate a silver wire quasi-reference electrode from the main chamber containing the OPG working electrode and a platinum wire counter electrode. The cell for the aqueous studies comprised a separate chamber for each electrode with a Luggin capillary extending from the reference chamber to the proximity of the OPG surface. For all aqueous experiments, the potential was measured versus a saturated calomel electrode (SCE).

Phthalocyanine solutions were prepared in DCB with

0.1 M TBAP as supporting electrolyte, such that the concentration was ca. 10 μM with respect to the TNPc unit. These solutions were purged with argon for about an hour before scanning the working electrode at a rate of 100 mV/s over the range 0.00 to +1.00 V versus the silver wire. Adsorbed layers on OPG or SAPG electrodes were obtained by cycling until the anodic and cathodic peak currents associated with the adsorbed species remained constant over five minutes of continuous scanning. When this condition was satisfied, the adsorbed layer was assumed to have reached a steady coverage. Scans at various rates were then recorded to determine the surface coverage (vide infra).

The catalytic efficiency of the various phthalocyanine compounds was investigated with the adsorbed species on the OPG electrode. This modified electrode was removed from the phthalocyanine solution, washed with ethanol, then with water, and finally placed in the cell for the aqueous studies. The 0.10 M NaOH solution in this cell had been purged with oxygen for several hours to ensure saturation. The electrode was then scanned over the range 0.00 to -1.00 V versus SCE at a rate of 10 mV/s for rotation rates ranging from 400 to 10,000 rpm. After each scan, the electrode was held at 0.00 V for 1 minute to permit the rotation rate to be changed for the next scan.

Results

I)Adsorption Studies

Some preliminary adsorption experiments were performed on a SAPG electrode to determine the electronic nature and orientation of the adsorbed species. The cyclic voltammograms for a solution of 2.5×10^{-5} M CoTNPc in DCB and 0.1 M TBAP studied at a SAPG working electrode, as shown in Figure 1, display two couples in close proximity. Following deconvolution of these waves (70), a plot (Figure 2A) of cathodic peak current, $i_{p,c}$, versus scan rate, v, for couple I (R = 0.999) and a plot (Figure 2B) of $i_{p,c}$ versus $\sqrt{v}$ for couple II (R = 0.998) indicated that these couples were adsorption and diffusion processes (71), respectively. From the relative positions of couples I and II, it follows that the adsorbed species binds most strongly in the reduced form associated with couple II (72), although the presence of a reductive adsorption wave indicates that the oxidized form associated with this couple also binds to the electrode. Couple II is associated with the ligand process $[Co(II)TNPc(-1)]^{+}/Co(II)TNPc(-2)$ (73) and therefore CoTNPc binds to the graphite surface most strongly as $Co(II)TNPc(-2)$. The binding between the CoTNPc and the SAPG electrode can be explained by π-π interactions between the phthalocyanine ring and the graphite lattice, if the CoTNPc is adsorbed flat to the

SAPG surface. This mode of adsorption has also been suggested in a similar investigation (41) by Yeager and coworkers who studied cobalt tetrasulphonate phthalocyanine (CoTSPc).

In addition to the electronic nature and orientation of the adsorbed molecule, the extent of coverage of the catalyst on the electrode surface must be known. Quantitative analysis requires the selection of an appropriate adsorption isotherm to describe the cyclic voltammetric response of the adsorbate. An adsorption isotherm describes the relationship between the concentrations of the adsorbate in the adsorption layer and in the bulk phase from which the adsorption takes place. Appropriate isotherms may also yield information about interactions between molecules in the adsorption layer.

The Langmuir isotherm was used to analyse the adsorption of CoTNPc on a SAPG electrode. This isotherm applies to systems in which there are no interactions between the adsorbed molecules (72). For systems which satisfy these conditions, the value of n may be calculated from the peak-width-at-half-height, $W_{1/2}$, from the expression

[1] $$n = \frac{2RT}{W_{1/2}F} \ln(3+2\sqrt{2})$$

The average value of n calculated in this fashion was 1.00±0.02 in excellent agreement with our expectation of a one-electron

process. By calculating the charge under the adsorption peak and assuming the area of a phthalocyanine molecule, A_{pc}, is 200 A^2 (41), the coverage of CoTNPc on a SAPG electrode was determined to be about 0.3±0.1 monolayers. This low level of coverage is consistent with another study (41) in which CoTSPc adsorbed on SAPG to the extent of 0.4 monolayers.

Since a coverage of between one and two monolayers was desired for these oxygen reduction studies, SAPG was not used for these investigations. (Recent studies have established a method for obtaining a coverage of one monolayer on SAPG which will be employed in later investigations.) Yeager and coworkers (42) found that CoTSPc could be adsorbed on OPG to about four times the coverage on SAPG; the greater adsorption on the OPG electrode was attributed to a higher density of surface defects assumed to be critical to adsorption (74). Adsorption experiments with CoTNPc and an OPG electrode did show enhanced adsorption, as shown in Figure 3. This increased adsorption affects the cyclic voltammograms in many ways. The most readily apparent effect is the loss of the diffusion wave which had been observed in conjunction with an adsorption wave when using SAPG. Since the adsorption wave overwhelms the diffusion wave under the conditions employed for this experiment (71), later calculations of surface coverage disregard contributions from diffusion and treat this as a pure

adsorption process. The other noticeable effect in Figure 3 is the large peak separation observed at higher scan rates. This probably arises from the larger currents observed in this scan and the high iR drop in these DCB solutions.

The adsorption studies with the OPG electrode were analysed with the Langmuir isotherm which gave an average n value of 0.72±0.04, suggesting that the use of the Langmuir isotherm was not appropriate for this system. An alternate choice, the Frumkin isotherm (75-78), is useful for systems in which there are interactions between adsorbed molecules. A recent investigation (78) of several isotherms suggests that the Frumkin isotherm is most appropriate for electrochemical processes involving the adsorption of organic compounds. According to the Frumkin isotherm, the peak current and the value of n are given by the expressions (77)

$$[2] \qquad i_p = \frac{n^2F^2A\Gamma v}{RT(4 - 2r\Gamma)}$$

$$[3] \qquad n = \frac{2RT}{W_{1/2}F}\left[\ln P - r\Gamma \frac{P - 1}{P + 1}\right]$$

where r is an interaction parameter (cm^2/mol), Γ is the surface concentration of the adsorbed species (mol/cm^2), and P is given by

$$[4] \qquad P = 3 - r\Gamma + \left(r^2\Gamma^2 - 6r\Gamma + 8\right)^{1/2}$$

Repulsive interactions are denoted by negative values of r

while stabilizing interactions are denoted by positive values of r. If the interactions between adsorbed molecules are repulsive, the wave broadens and the peak decreases, but if the interactions are attractive, the wave narrows and the peak increases. If the interaction parameter is zero, then the Frumkin isotherm expressions simplify to those given by the Langmuir isotherm.

The cyclic voltammograms from the adsorption studies on OPG displayed waves which were broader and more rounded than those observed for the SAPG experiments. This change in waveshape indicates that at these higher coverages, repulsive interactions exist between molecules adsorbed on the electrode surface. The voltammograms which had been analysed by the Langmuir isotherm to give an average n value of 0.72 ± 0.04 when analysed by the Frumkin isotherm yielded 0.93 ± 0.03 in much better agreement with the expected value of unity.

Average values of the dimensionless parameters $r\Gamma$ and the average surface coverage, θ, (where $\theta = \Gamma A_{pc}$) are presented in Table 1 for an OPG electrode modified with CoTNPc or one of its binuclear derivatives. The surface coverage calculations for the binuclear compounds used the same area approximation per phthalocyanine unit as had been used for CoTNPc since these calculations were designed to estimate the number of cobalt atoms on the electrode surface, not the number of

phthalocyanine molecules. As a means of clarifying this point, consider the following example. If a value of 2.0 is calculated for θ, this could indicate that the electrode is covered by two monolayers of the mononuclear species, two layers of a binuclear species in an 'open' configuration, or one layer of a binuclear species in a cofacial configuration. Consideration of steric restraints in these molecules and the behaviour of these species in solution is required to infer the manner in which these molecules adsorb on the electrode surface.

The θ value of 1.4±0.4 for CoTNPc-modified OPG electrodes is most likely indicative of a coverage of one monolayer. The reported θ may be somewhat high as it is based on the geometric area of the electrode and does not account for the inherent roughness of the surface. It is improbable that a second layer forms on the surface since none of the adsorbate is lost after washing and transferring to an aqueous solution. A weakly bound second layer of CoTSPc on OPG has been reported (74), but it was readily removed by washing.

The average coverage for the molecule $O(1)[CoTrNPc]_2$ was 1.3±0.4, which is quite similar to that found for CoTNPc. The adsorption of $O(1)[CoTrNPc]_2$ was anticipated to be similar to that of CoTNPc because this binuclear species can only exist in

an 'open' conformation. The $O(1)[CoTrNPc]_2$ molecule would adsorb with one ring flat on the OPG surface while the other ring lies at some oblique orientation. The ring in the oblique orientation would give this surface a highly disordered structure and, from the rΓ value in Table 1, it would appear that it also leads to abnormally high repulsive interactions.

The remaining binuclear phthalocyanines have average θ values near two. If these molecules adsorbed on to the electrode surface in an 'open' conformation then a θ value near two would not be expected since, as noted earlier, the Π-Π interactions which arise between the first and second layer of phthalocyanine molecules adsorbed on the electrode surface are too weak to stabilize a second layer. It would therefore appear that most of these binuclear species adsorb on to the electrode surface in some sort of cofacial arrangement. This configuration is easily obtained by $Cat(4)[CoTrNPc]_2$ and $EtMeO(5)[CoTrNPc]_2$, but the stacking of $C(2)[CoTrNPc]_2$ would necessitate that the phthalocyanine rings in the second layer lie above a surface bound ring of an adjacent $C(2)[CoTrNPc]_2$ molecule. The values of rΓ reported for these binuclear compounds are fairly consistent and are quite similar to the value of -0.7 reported by Collman and Anson (28) for one of their cofacial cobalt porphyrins. It has been suggested that the source of repulsions observed for flatly adsorbed aromatic

molecules such as these, is the parallel orientation of their dipoles (79).

Another interesting feature of these adsorption studies is illustrated in Figure 4. The cyclic voltammograms for O(1)[CoTrNPc]$_2$ and Cat(4)[CoTrNPc]$_2$ display one adsorption wave for the [Co(II)TrNPc(-1)]$^+$/Co(II)TrNPc(-2) couple, just like that observed for the adsorption of CoTNPc on OPG (see Figure 3). However, the cyclic voltammograms for C(2)[CoTrNPc]$_2$ and EtMeO(5)[CoTrNPc]$_2$ display two couples in the same potential region. Plots of i_p versus ν for the two couples are linear, thus both couples arise from adsorption processes. Frumkin isotherm analysis yielded values of n close to unity which, when combined with the potential of these couples, suggests that these couples are both associated with the [Co(II)TrNPc(-1)]$^+$/Co(II)TrNPc(-2) process. The origin of these two adsorption processes may be explained in terms of the electronic coupling inherent in these binuclear compounds.

The theory of intramolecular coupling in these binuclear phthalocyanines has been presented elsewhere (66). In solution, these binuclear species are expected to exist in a dynamic equilibrium between various conformations, dependent upon the nature of the bridge since, in some cases, steric effects may provide barriers to free rotation. Therefore, the

electronic absorption spectrum of a solution of one of these binuclear species would represent the summation of the spectra of a mixture of these conformers. The coupling in these species resulted in a blue-shifted Q band which was also broadened, the degree of this broadening being a qualitative measure of the degree of electronic coupling in these binuclear species.

The half-bandwidths of the five phthalocyanine species investigated in this study are presented in Table 2 (80). The relative extent of coupling in these compounds, as established by these half-bandwidths, is as follows:

[5] $O(1)[CoTrNPc]_2 > EtMeO(5)[CoTrNPc]_2 \simeq Cat(4)[CoTrNPc]_2 >$
$C(2)[CoTrNPc]_2 > CoTNPc$
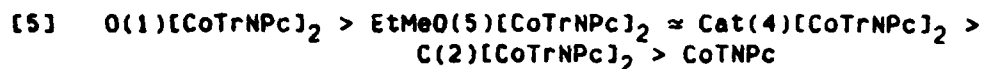
Cyclic voltammograms of each of the binuclear species are presented in Figure 4. In the voltammograms of $C(2)[CoTrNPc]_2$ and $EtMeO(5)[CoTrNPc]_2$, two adsorption waves are observed which arise from two distinct redox couples in close proximity. Similar voltammograms have been reported previously (28,81) but, in these earlier reports, both of the redox processes could be observed when the species was in solution, not bound to the electrode surface. For each of the adsorbed binuclear species, one phthalocyanine ring lies on the electrode surface while the other ring is not in contact with it. The two redox couples, therefore, are regarded to arise from the bound Pc

ring, and the bridged Pc ring which is not bound directly to the electrode. In solution, only one redox process is observed, common to both rings. In the more highly coupled species, namely $O(1)[CoTrNPc]_2$ and $Cat(4)[CoTrNPc]_2$, electron transfer across the bridge to the outer phthalocyanine ring is facile and therefore only one redox couple is observed. However, electron transfer across the saturated $C(2)[CoTrNPc]_2$ and $EtMeO(5)[CoTrNPc]_2$ bridges is inhibited and therefore the redox potential for the outer phthalocyanine ring could differ from that of the inner phthalocyanine ring. Although the $O(1)[CoTrNPc]_2$ bridge is, technically, also a saturated bridge, it is apparent from the half-bandwidth studies mentioned above, that electron transfer across this bridge is permissible. This proposal could explain the differences between the cyclic voltammograms given in Figure 4, although further study would be necessary to establish the source of this behaviour conclusively.

II)Oxygen Studies

The catalytic properties of these phthalocyanine species were investigated by means of rotating disc electrode (RDE) studies. The diffusion-limited current for such an experiment, expressed in mA, is described by the expression (82)

$$[6] \quad i_L = 1000nAFC\left(\frac{2\pi U\omega}{60}\right)^{1/2}\left[\frac{0.6204 S^{-2/3}}{1 + 0.2980 S^{-1/3} + 0.14514 S^{-2/3}}\right]$$

where U is the kinematic viscosity (cm^2/s), ω is the rotation rate (rpm), S is the Schmidt number ($S = U/D$), A is the electrode area (cm^2), F is Faraday's constant, and C is the concentration of O_2 (mol/cm^3). A Levich plot $\left(i_L \text{ versus } \omega^{1/2}\right)$ of the diffusion-limited O_2 reduction current at a CoTNPc-modified OPG electrode is shown in Figure 5. In the calculation of i_L for this Levich plot, the diffusion coefficient and concentration of O_2 were taken as 1.67×10^{-5} cm^2/s (42) and 1.38×10^{-6} mol/cm^3 (83), respectively, the kinematic viscosity was estimated at 9.97×10^{-3} cm^2/s (84), the Scmidt number was calculated to be 597, and the value used for n was two. The good agreement between the calculated diffusion-limited current and the experimentally observed limiting current suggests that O_2 is undergoing a two-electron reduction to peroxide rather than a four-electron reduction to water. Further evidence for this two-electron reductive pathway will be presented later.

If an electrode process is hindered by a kinetic step, a plot of i_L, or i, versus $\omega^{1/2}$ deviates from the linear relationship given in equation 6 (71). The effect of this kinetic step on the current that flows in the potential region of mixed diffusion-kinetic control for a first-order process under steady-state conditions is given by the expression

(86-88):

[7] $\qquad 1/i = 1/i_k + 1/i_L$

in which i_k is the kinetically-limited current. A plot of $1/i$ versus $1/\omega^{1/2}$, known as the Koutecky-Levich plot, establishes this kinetically-limited current which is equivalent to the current that would flow if the concentration of O_2 at the electrode surface could be maintained at its bulk concentration during the reduction process. Therefore, i_k at a given potential is directly proportional to the maximum rate at which O_2 can be reduced to peroxide at the catalyst-modified electrode at that potential (89).

The reduction of O_2 at an OPG electrode modified with CoTNPc is shown in Figure 6. These scans were recorded at 10 mV/s, but may be considered to be steady-state curves since no hysteresis was observed between the forward and reverse scans. Following the procedures presented by Frumkin and Tedoradse (90), Koutecky-Levich plots at -0.450 V, -0.500 V, -0.550 V and -0.600 V were constructed. Koutecky-Levich plots of O_2 reduction at -0.450 V for OPG electrodes modified with CoTNPc and each of its binuclear derivatives are given in Figure 7. The scatter for Koutecky-Levich plots was small (R > .999) and the n values calculated from the slopes of these plots (Table 3) were consistent with a two-electron process yielding peroxide as the reduction product. The different

intercepts for the Koutecky-Levich plots illustrate that the catalytic activity of these species differ. The kinetically-limited currents for oxygen reduction are presented in Table 4. These kinetically-limited currents have been normalized to the CoTNPc data to rank the catalytic efficiency of the binuclear species and these normalized kinetically-limited currents are presented as the bracketed values in Table 4. The standard deviation for the average normalized kinetically-limited currents is less than 15% which though somewhat large, is similar to the deviation reported in another study (91). These normalized currents indicate the reactivities of these species towards oxygen reduction are as follows:

[8] $O(1)[CoTrNPc]_2 > EtMeO(5)[CoTrNPc]_2 \simeq Cat(4)[CoTrNPc]_2 >$
$$C(2)[CoTrNPc]_2 > CoTNPc$$
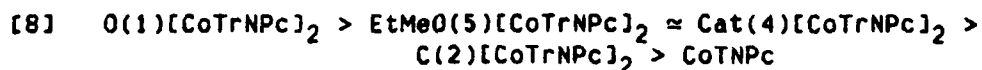
It is surely significant that this ranking is the same as given for the electronic coupling of these species.

Although the binuclear CoTNPc compounds have shown increased activity towards the electrocatalytic reduction of molecular oxygen, the potential at which this process occurs in pH 13 NaOH solution is approximately the same as that for CoTSPc under the same conditions (41), and rather too negative to be practical for a fuel cell catalyst. Present studies are being directed towards the shifting of the molecular oxygen reduction potential to more positive values by performing

these experiments under acidic conditions, and also to devise conditions under which the direct four-electron reduction process will be favoured.

Summary

In basic media, binuclear cobalt phthalocyanines were shown to be more active towards the electrocatalytic reduction of molecular oxygen than the corresponding mononuclear species. The increased activity of these binuclear compounds has been attributed to the increased electronic coupling between the phthalocyanine rings of these species. Current studies include CoPc species showing a much greater degree of intramolecular coupling than observed here (92). A mechanistic study of CoTNPc over the pH range 1 to 13 will also be reported shortly.

Acknowledgements

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Figure Legends

Figure 1 Cyclic voltammograms at scan rates of a) 50 mV/s, b) 100 mV/s, and c) 150 mV/s for 2.5 X 10^{-5} M CoTNPc in DCB and 0.1 M TBAP under argon at a SAPG working electrode. Couples I and II are both associated with the $[Co(II)TNPc(-1)]^+$/Co(II)TNPc(-2) process. The nature of these couples is investigated more fully in Figure 2.

Figure 2 Plots of the dependence of cathodic peak current with scan rate for A) couple I and B) couple II, as designated in Figure 1. (2.5 X 10^{-5} M CoTNPc in DCB and 0.1 M TBAP at a SAPG working electrode).

Figure 3 Cyclic voltammograms at scan rates of a) 50 mV/s, b) 100 mV/s, and c) 150 mV/s for 1.0 X 10^{-5} M TNPcCo in DCB and 0.1 M TBAP at an OPG working electrode. The waves shown here are associated with the $[Co(II)TNPc(-1)]^+$/Co(II)TNPc(-2) couple.

Figure 4 Cyclic voltammograms displaying adsorption features of a) $O(1)[TNPcCo]_2$, b) $Cat(4)[TNPcCo]_2$, c) $C(2)[TNPcCo]_2$, and d) $EtMeO(5)[TNPcCo]_2$. All voltammograms were recorded at a scan rate of 100 mV/s for a binuclear concentration of ca. 5 μM in DCB and 0.1 M TBAP. The waves shown here are associated with the $[Co(II)TNPc(-1)]^+$/Co(II)TNPc(-2) couple.

Figure 5   Levich plot of the diffusion-limited O_2 reduction current at a CoTNPc-modified OPG electrode.   The dashed line is the   response   predicted by equation [6] and the solid line   is the fit through the experimental data denoted by +'s.

Figure 6   Reduction   of molecular oxygen at   a   rotating   OPG electrode   modified   CoTNPc   in   an O_2 saturated   0.10   M   NaOH solution.

Figure 7   Koutecky-Levich plots for the reduction of   molecular oxygen   in 0.10 M NaOH at -0.450 V versus SCE on OPG electrodes modified   with □ CoTNPc,   + O(1)[CoTrNPc]$_2$,   ♦   C(2)[CoTrNPc]$_2$, Δ Cat(4)[CoTrNPc]$_2$, or X EtMeO(5)[CoTrNPc]$_2$.   A theoretical two electron   line   is   shown   at   the   bottom   of   the   graph   for comparison.

Compound	θ	$r\Gamma$
CoTNPc	1.4±0.4	-0.77±0.14
O(1)[CoTrNPc]$_2$	1.3±0.4	-1.36±0.11
C(2)[CoTrNPc]$_2$	1.8±0.1	-0.87±0.13
Cat(4)[CoTrNPc]$_2$	2.2±0.2	-0.88±0.06
EtMeO(5)[CoTrNPc]$_2$	2.2±0.4	-0.85±0.01

Table 1 Average values of θ and $r\Gamma$ for an OPG electrode modified with CoTNPc or one of its binuclear derivatives.

Compound	Half-Bandwidths (cm^{-1})	
	Co(III)	Co(I)
CoTNPc	680	660
C(2)[CoTrNPc]$_2$	765	735
Cat(4)[CoTrNPc]$_2$	800	775
EtMeO(5)[CoTrNPc]$_2$	785	775
O(1)[CoTrNPc]$_2$	1000	920

Table 2 Half-bandwidths of the Q band for CoTNPc and its binuclear derivatives as Co(III) and also as Co(I). These half-bandwidths were calculated from the spectra obtained by bulk electrolysis of DCB solutions containing these species along with an excess of tetrabutylammoniumhydroxide and 0.1 M TBAP [80].
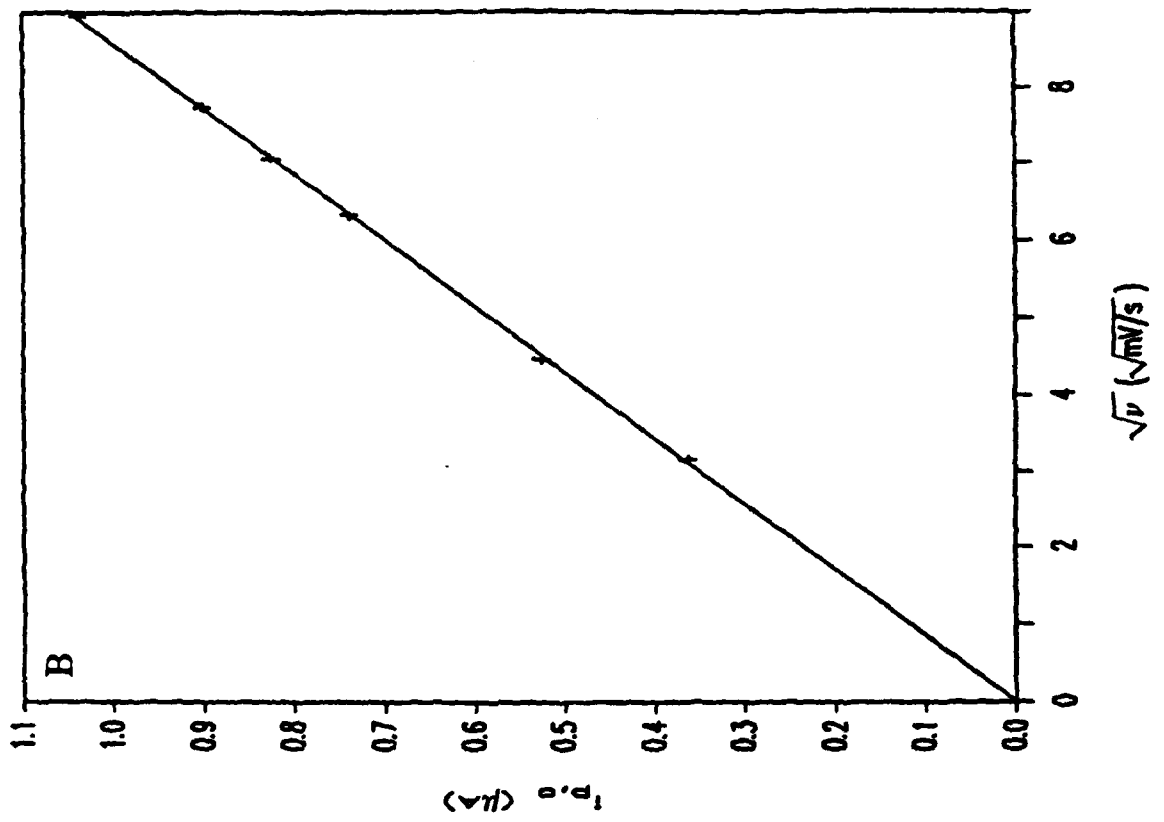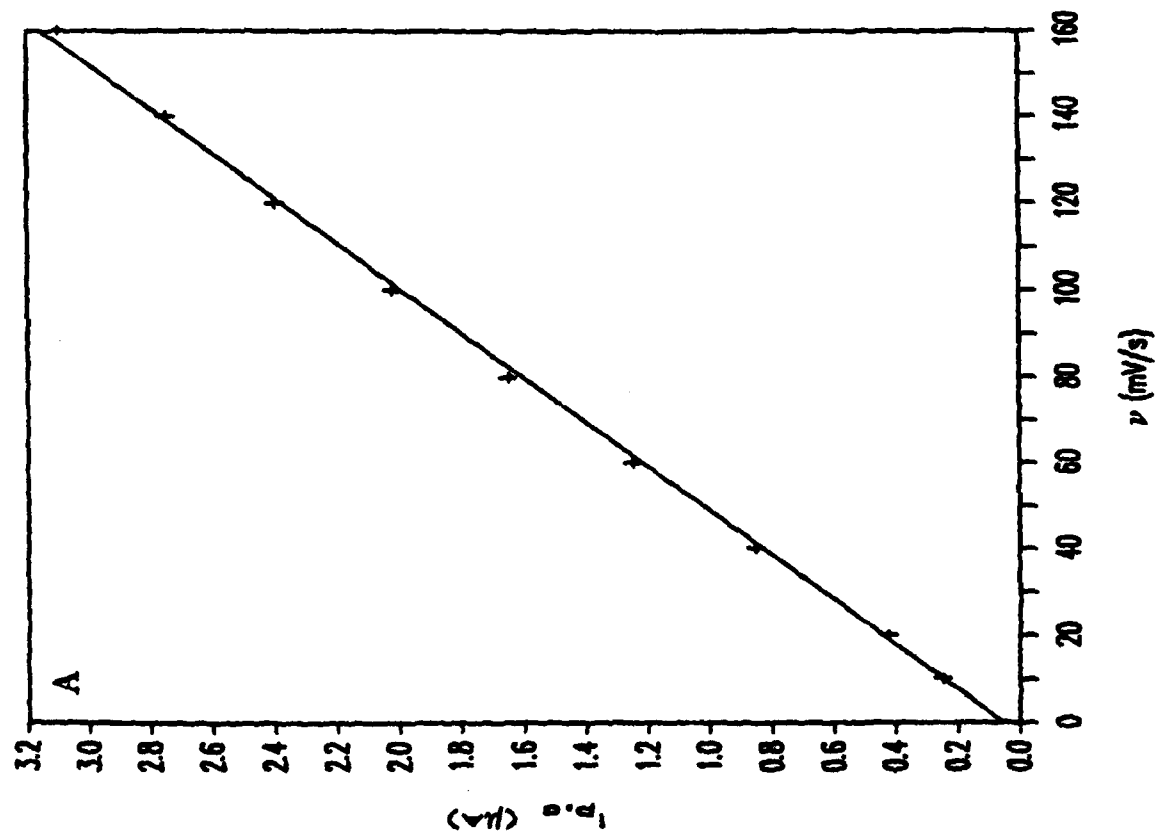
Compound	n			
	Potential (Volts versus SCE)			
	-0.450	-0.500	-0.550	-0.600
CoTNPc	1.94±0.17	1.93±0.11	1.91±0.10	1.93±0.06
O(1)[CoTrNPc]$_2$	2.07±0.02	2.04±0.02	2.02±0.02	2.01±0.01
C(2)[CoTrNPc]$_2$	2.09±0.01	2.05±0.01	2.01±0.01	1.99±0.02
Cat(4)[CoTrNPc]$_2$	2.10±0.09	2.03±0.01	1.99±0.01	1.98±0.02
EtMeO(5)[CoTrNPc]$_2$	1.94±0.01	1.94±0.02	1.94±0.01	1.96±0.01

Table 3 Average values of n for the electrocatalytic reduction of oxygen in 0.10 M NaOH at an OPG electrode modified with CoTNPc or one of its binuclear derivatives.
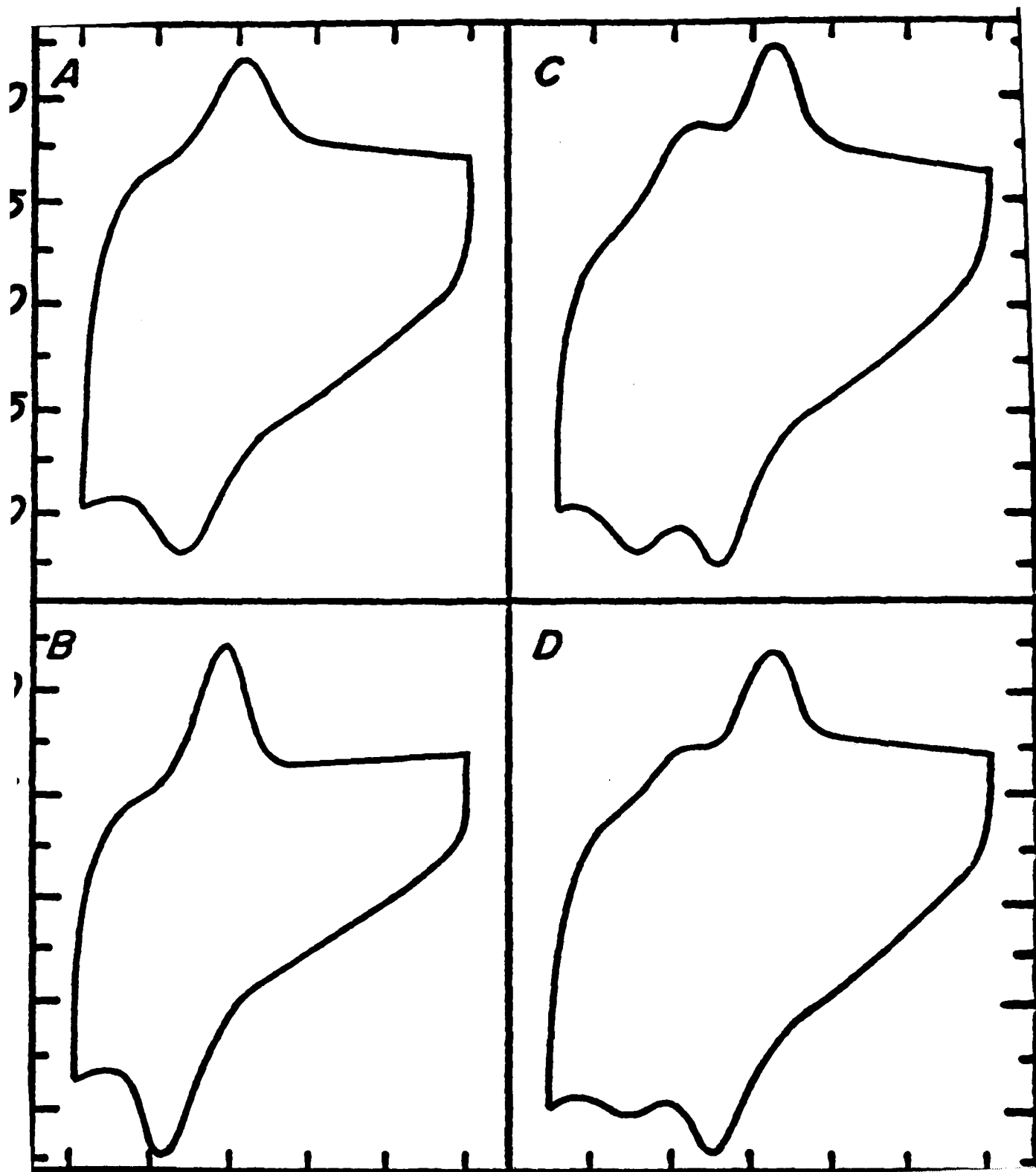
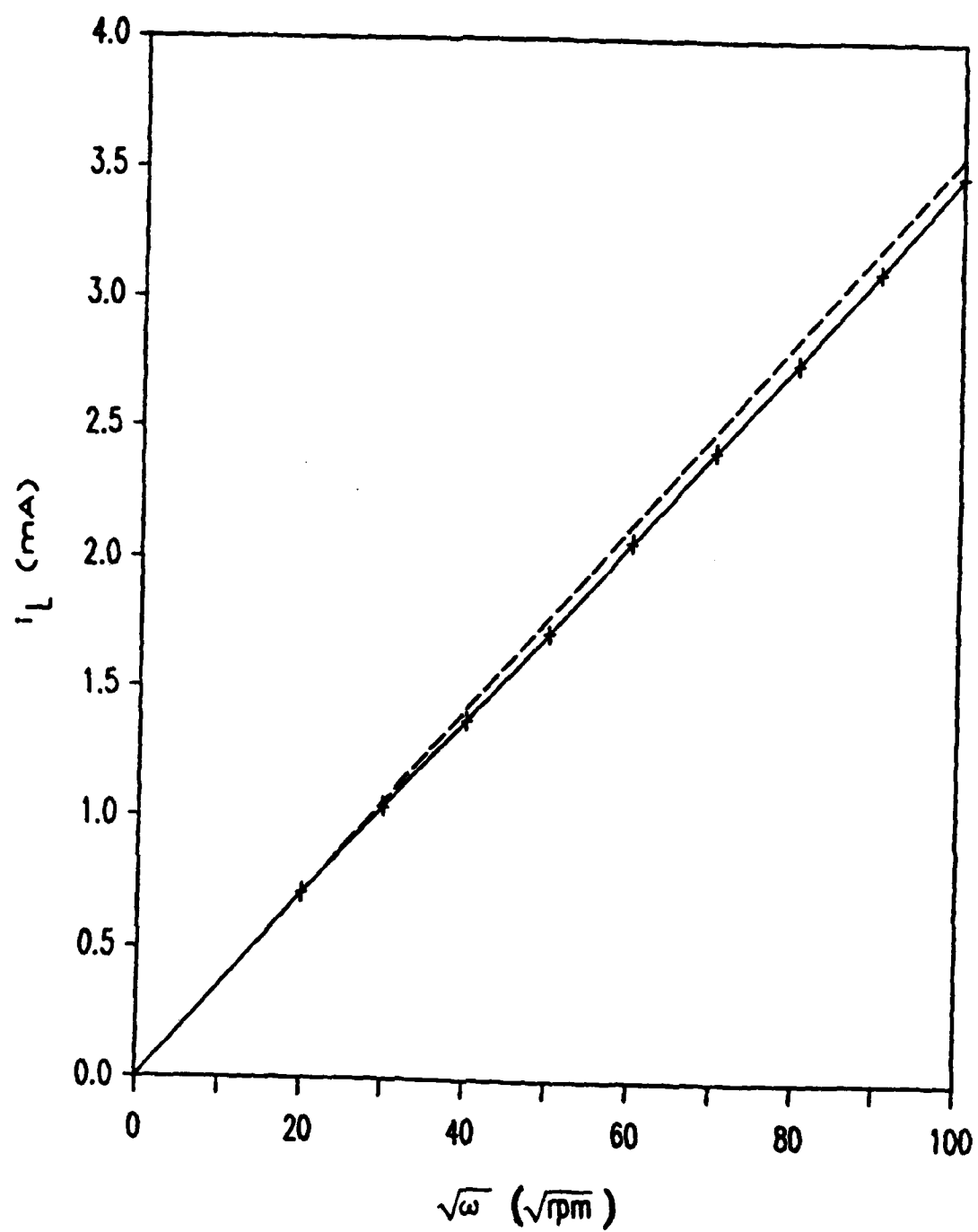| Compound	Potential (Volts versus SCE)				Average Normalized i_k
	-0.450	-0.500	-0.550	-0.600	
CoTNPc	1.51 (1)	3.00 (1)	5.58 (1)	9.95 (1)	-
C(2)[CoTrNPc]$_2$	1.64 (1.09)	3.20 (1.07)	5.90 (1.06)	11.01 (1.11)	1.08±0.02
Cat(4)[CoTrNPc]$_2$	1.84 (1.22)	3.91 (1.30)	7.95 (1.42)	16.01 (1.61)	1.39±0.17
EtMeO(5)[CoTrNPc]$_2$	2.35 (1.56)	4.38 (1.46)	7.68 (1.38)	13.08 (1.31)	1.43±0.10
O(1)[CoTrNPc]$_2$	2.45 (1.62)	4.61 (1.54)	8.15 (1.46)	13.89 (1.40)	1.50±0.10

Table 4 Kinetic currents, in mA, and normalized kinetic currents (in brackets) for oxygen reduction in 0.10 M NaOH at OPG electrodes modified with CoTNPc or one of its binuclear derivatives. (Electrode area = 0.493 cm^2)
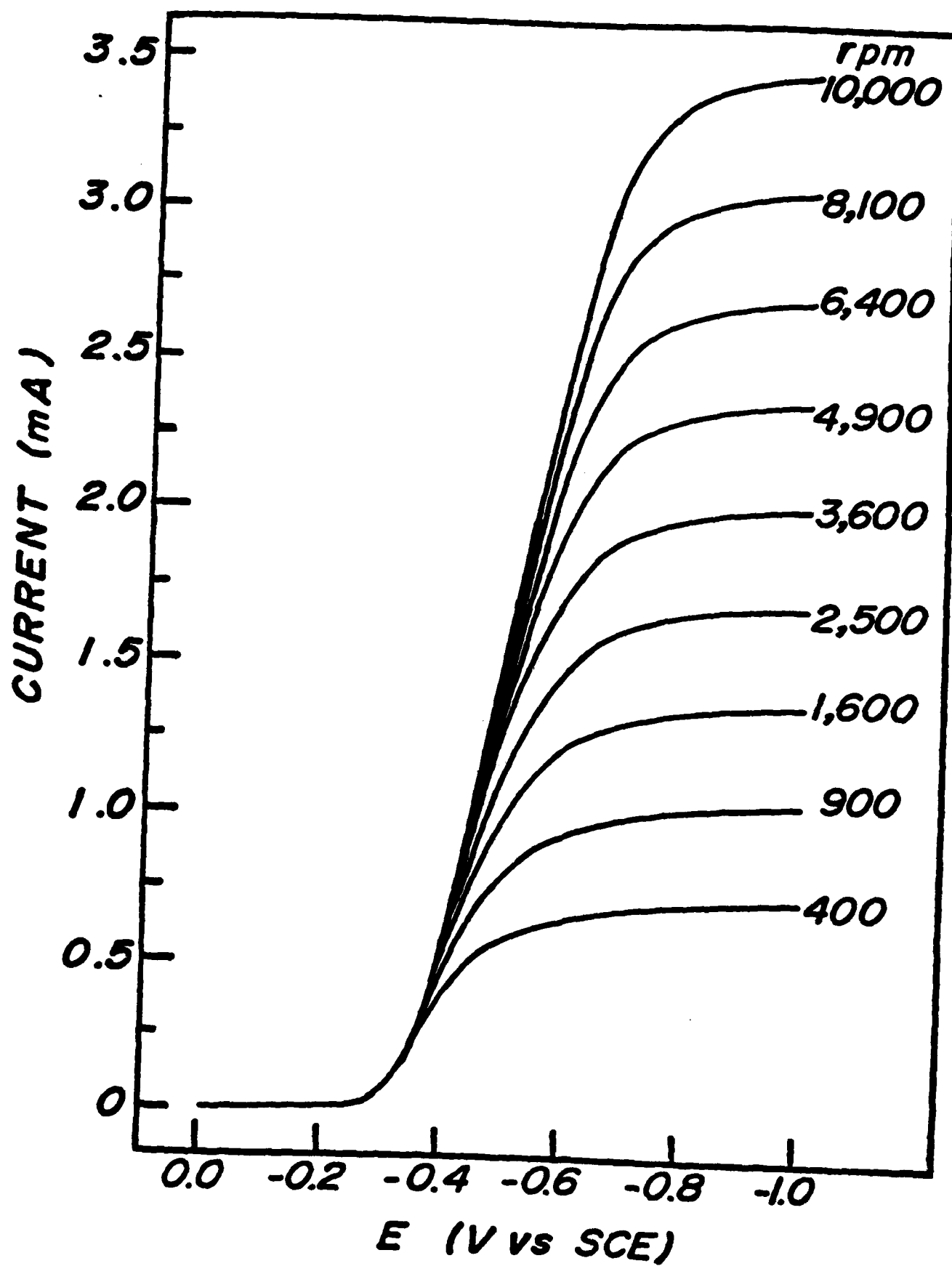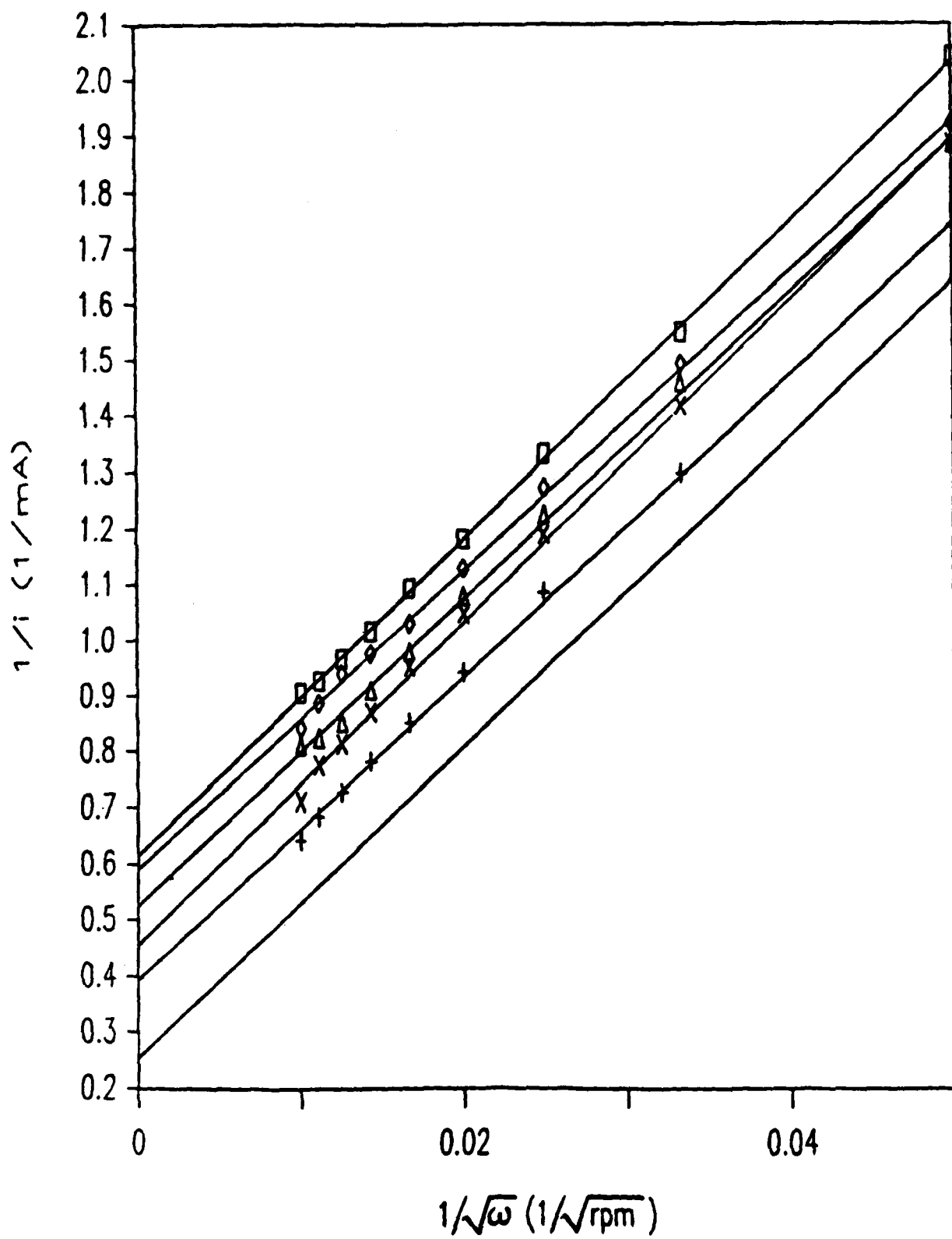
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