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Electrochemical and Solid State Studies of Phthalocyanine Thin Film Electrodes

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Abstract: Electrochemical studies have been made of phthalocyanine surfaces. The electrodes were fabricated by evaporating 70 Å of chromium, 300 Å of gold, and ~3000 Å of a phthalocyanine, in sequence, onto a glass substrate in vacuo. Metal-free, zinc, iron(II), and copper phthalocyanines (H_2Pc, ZnPc, FePc, and CuPc) were examined. ZnPc and FePc electrodes showed a capacity for nearly reversible charge transfer reactions on a cyclic voltammetric time scale, and this Faradaic activity could be assigned to the phthalocyanine surfaces themselves. Parallel experiments with gold/phthalocyanine/gold sandwich devices highlighted the importance of water and oxygen for introducing appreciable electronic conductivity into the phthalocyanine phases. These ambient effects on the bulk phases were mirrored in the voltammetric responses of the phthalocyanine electrodes. ZnPc and FePc surfaces could not efficiently mediate electrode reactions (including O_2 reduction) that occurred on Au at potentials more negative than 0.0 V vs. SCE, whereas reactions in the positive region proceeded readily. Several of the inhibited reactions could be photoassisted on ZnPc. The results are generally in accord with a view of the phthalocyanines as fairly well behaved p-type semiconductor electrodes having flat-band conditions near 0.0 V vs. SCE.

Electrochemical reactions at chemically modified surfaces have attracted much attention lately, because they may be useful in promoting catalytic or selective electrode processes.[2-22] Surface-linked chromophores have also been used to extend the spectral responses of semiconductor photoelectrodes to longer wavelengths.[13] Besides serving these practical ends, surface-modified electrodes represent some interesting new tools for fundamental studies of electron-transfer reactions.

In most published work along this line, elegant chemical steps have been used to bond electron or photon mediators to a surface at roughly monolayer coverage. An alternative approach to new and chemically interesting electrode surfaces is to enable Faradaic reactions to occur directly on molecular solids. This option has not been explored to any great extent, because the bulk conductivities of such materials are usually low, hence they cannot be used for electrodes of conventional dimensions. Molecular phases with metallic conductivity provide the exceptions to this rule, and recent work by Nowack et al. with polymeric sulfur nitride, $(SN)_x$, has opened the way to further research with massive molecular electrodes made from highly conductive materials.[23]

Other substances can be fabricated into useful electrodes by employing thin film technology. A thickness on the order of 1000 Å deposited over a metallic conductor can provide a current path of sufficiently low resistance, even with bulk resistivities in the overlayer as high as 10^8 ohm cm. Our concern here is with electrodes of this type made from various phthalocyanines.

The phthalocyanines have received much attention in electrochemistry since 1964, when Jasinski reported that several of them could catalyze the electroreduction of oxygen in aqueous media.[24,25] Electrodes of many types have been fabricated.[24-43] Powdered carbon or metal has been coated with the phthalocyanines by chemical vapor deposition, solvent evaporation, and electrophoretic deposition. These same powders have also been pressed with crystalline phthalocyanines into composite electrodes. Bulk metal surfaces have been coated by solvent evaporation, by adsorption from solution, and, in relatively few cases, by deposition of the phthalocyanine by evaporation in vacuo. Virtually all of the reported studies were devoted to the catalysis of oxygen's electroreduction. Catalysis was frequently observed, but in most of this work it has been difficult to discern whether the Faradaic process actually occurs on the phthalocyanine or, instead, takes place on the conducting support while being facilitated by ancillary heterogeneous reactions on nearby phthalocyanine surfaces.[31,41]

However, several recent investigations have given strong indications that the phthalocyanine surfaces are indeed capable of Faradaic reactions. Appleby and Savy have made careful studies of the kinetics of O_2 reduction,[39,41] and they have observed markedly different pH dependences for Tafel slopes recorded for coated and uncoated carbon powders. These authors have also done very extensive spectroscopic and electrochemical work with thin films of phthalocyanines on planar substrates, and they have discussed detailed hypotheses about the chemical basis for the observed electrocatalysis.[37,39,41] Alferov and Sevast'yanov observed photoinduced reduction of O_2 on several phthalocyanines that were evaporated to 100–1000 Å thicknesses on polished graphite.[36] The origin of the photoeffect was not explained in detail, but it may manifest semiconductor-based photoelectrochemical properties of the phthalocyanines. More recently, Meshitsuka and Tamura have observed photoinduced oxidation of oxalate on 10 000 Å thick films of CuPc deposited over Pt.[40] Their results could be quantitatively interpreted in terms of Faradaic activity on the outer surface of CuPc, which behaved like an intrinsic semiconductor.

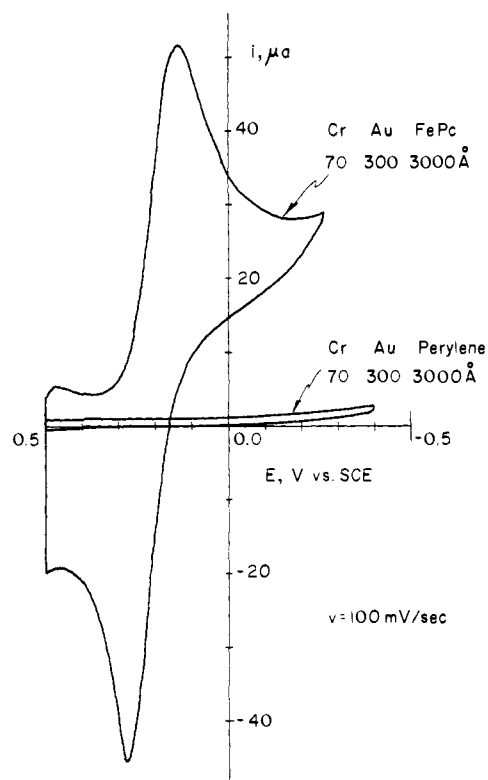Our interest here is with the more general electrochemical

Figure 1. Cyclic voltammograms of 1 mM $Fe(CN)_6^{3-}$ in 0.1 M KNO_3.

Figure 2. Cyclic voltammograms of 1 mM $Fe(CN)_6^{3-}$ in aerated 0.1 M KNO_3.

behavior of phthalocyanine thin film electrodes. We shall show below that they are indeed capable of Faradaic reactions and that nearly reversible electrode kinetics are possible. At the same time, there is evidence for chemical selectivity in the processes that can be observed. Quite surprisingly, oxygen is not reduced significantly on our films. The solid-state properties of the films strongly influence electrochemical performance, and those properties depend markedly on the ambients to which the electrode has been exposed.

Experimental Section

Thin films of metals and phthalocyanines were prepared by evaporation using a Varian Model 3117 vacuum bell jar system. Depositions were carried out at pressures between 10^{-5} and 10^{-6} Torr, and thicknesses were gauged by a Sloan Model 200 quartz crystal monitor.[44]

Phthalocyanine thin film electrodes were prepared on microscope cover glasses, which were 25 mm square and had a thickness of 0.1 mm. They were cleaned by successive washings in aqua regia, aqueous detergent, distilled water, and absolute ethanol; then they were dried at 100 °C in air. Before placement of a plate in the vacuum system, static charge and dust were removed from its surface by an ionized nitrogen jet stream from a Simco static eliminator. Finally, the plate was exposed to a glow discharge in air during pumpdown.

The electrodes actually comprised three-layer assemblies. First, a thin chromium film (70 Å) was deposited as an adhesive layer to improve the physical strength of the electrodes in solution. This layer was evaporated through a mask that left metal on the substrate in a T-shaped pattern. In the center was a disk having an area of 0.2 cm², and along one whole substrate side was a bus bar for contact. A smaller bus line connected the disk to the bar at its midpoint. This chromium shape was covered precisely in the next processing step by a 300-Å gold layer evaporated through the same mask. Finally, the phthalocyanine film was deposited onto the gold. For this step, the substrate was masked so that the phthalocyanine covered its entire surface except for the bus bar along the edge. The various phthalocyanines were purchased from Eastman Kodak and were used without further purification. They were deposited from a quartz crucible placed in a shielded crucible heater (Sylvania Emissive Products). The crucible was generally heated at 220 °C for 1 h before the temperature was
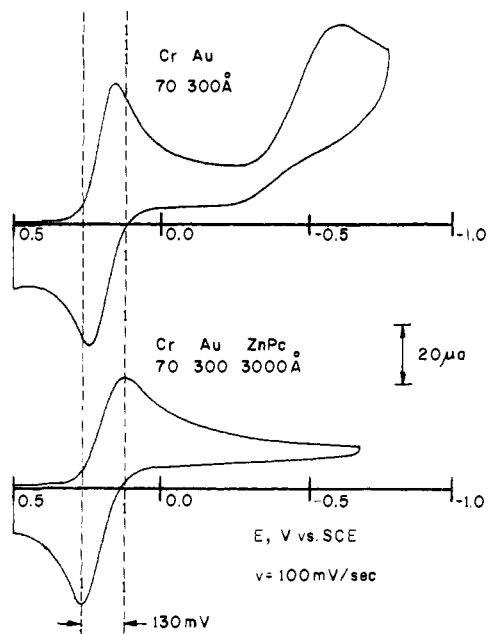
raised to start deposition. A shutter was held over the sample until the temperature exceeded 420 °C.

Sandwich cells for conductivity studies were prepared in a similar manner. The substrates were Pyrex glass plates ($1 \times 1 \times \frac{1}{16}$ in.) which were cleaned as described above, except that the ethanol rinse was replaced by an exposure to 2-propanol in a vapor degreaser. A chromium layer was not deposited. Instead, a 300-Å-thickness of gold was evaporated directly onto the glass in the T-shaped pattern described above. The phthalocyanine deposition followed; then a second gold layer, having a thickness of 300 Å, was put down. This second layer was evaporated through the usual mask, but the image was rotated 180° with respect to its position for the lower gold layer. The Au/phthalocyanine/Au sandwich region then comprised a circular zone in the center of the plate. Bus bars on opposite sides allowed contact via clamps which covered their entire areas.

In electrochemical studies, the thin film electrodes were inserted into the solution only so far as to cover the disk region. A platinum foil or wire was used as an auxiliary electrode, and a saturated calomel electrode was used as a reference. Cyclic voltammetric measurements were made with a potentiostat and a waveform generator that were custom built from operational amplifiers.

For chronocoulometry, the potential program was generated by a Data General Nova 820 computer, which acted through a 12-bit D/A converter driving an auxiliary input to a Princeton Applied Research Model 173 potentiostat. The charge passed during electrolysis was integrated in the analog domain by an operational amplifier whose output was monitored by an 8-bit A/D converter. Chronocoulometric curves were sampled at even intervals on a variable time scale ranging from 10 μs/point to 10 ms/point. The digitized curves were displayed, either directly or as Anson plots,[45] on an oscilloscope driven by parallel 8-bit D/A converters.

The current-voltage characteristics of sandwich cells were measured in a nitrogen atmosphere, in the dark, and at room temperature. Application of voltages to the cells and observation of the currents were accomplished with the potentiostatic apparatus used for cyclic voltammetry.

Results and Discussion

The Site of Faradaic Activity. Electrochemical studies of several phthalocyanine electrodes were carried out by cyclic voltammetric and potential step techniques. Voltammetry at ZnPc and FePc surfaces yielded nearly reversible responses for the ferri-/ferrocyanide redox couple in neutral media. Figures 1 and 2 show typical traces. In general, the curves recorded with the ZnPc and FePc electrodes had slightly wider peak separations and slightly smaller peak currents than cor-
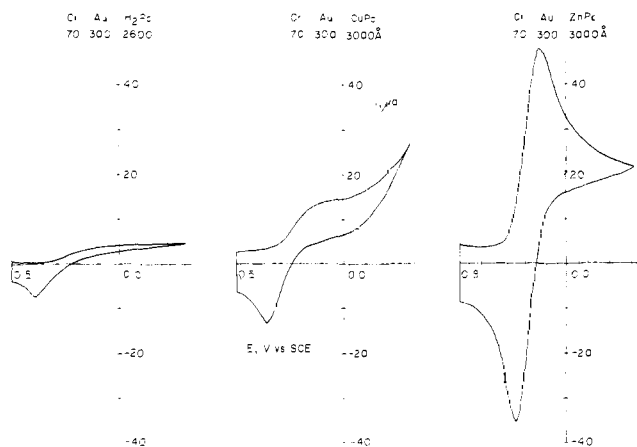
Figure 3. Cyclic voltammograms at various phthalocyanine electrodes. Scans begin at 0.5 V and move negatively at 100 mV/s. The solution was 1 mM $Fe(CN)_6{}^{3-}$ in 0.1 M KNO_3.

Table I. Data from Chronocoulometric Experiments[a]

| electrode | 0.05 V ⇌ 0.35 V[b] | | 0.0 V ⇌ −0.4 V[b] | |
	forward, μC	reverse, μC	forward, μC	reverse, μC
Au[c]	0.52	0.63	0.54	0.60
FePc[d]	0.28	0.25	0.28	0.30
ZnPc[d]	0.25	0.13	0.04	0.04

[a] With deaerated 0.1 M KNO_3. [b] Potential limits for step experiments. [c] Charges measured 1 ms after step. [d] Charges measured 2 ms after step. Overlayer thickness, 3000 Å.

responding voltammograms recorded from a bare gold disk like that underlying the phthalocyanine layers. These results seem to be the first showing virtually reversible charge transfer at phthalocyanine electrodes; thus it is important now to define the location of heterogeneous charge transfer as surely as possible.

There are two possibilities. Either the phthalocyanine is a conductor capable of fast interfacial electron transfer or it is effectively an insulator with channels or pinholes into which the solution penetrates, so that charge transfer can take place on the surface of the gold underlayer.

The voltammograms in Figures 1 and 2 demonstrate clearly that the diffusion fields determining the currents at ZnPc and FePc have the same area as that controlling the response at the bare gold disk. However, this fact alone cannot rule out the possibility of charge transfer via diffusion through pinholes, because a large number of channels distributed over a surface of area A will eventually merge their individual diffusion fields into a common field of cross section A, even though their combined exposed area is much less than A.[46] The time of merger will be roughly the time when the thickness of the diffusion layer becomes comparable to the spacing between pinholes. Experiments with time scales similar to those of our cyclic voltammograms involve diffusion layers of ~50 μ; hence pinholes spaced a few microns apart could give rise to voltammograms reflecting diffusion fields as large as the underlayer of gold. Other evidence must be used to establish the site of charge transfer.

Several independent observations bear on this issue. First, we note that voltammograms at CuPc, MgPc, and metal-free phthalocyanine (H_2Pc) were very distorted and showed small peak currents. Figure 3 displays typical results. The crystal structures and deposition characteristics of the various phthalocyanines are extremely similar,[47-50] so it is difficult to rationalize the voltammetric behavior in terms of differing tendencies toward pinhole formation. Moreover, the shapes of the waveforms, which always involve broad responses for reductions and sharp ones for oxidations, apparently manifest a kinetic aspect that is not easily related to a variable cross section for the diffusion field.

Another kind of experimental evidence that supports the idea of electroactive phthalocyanine surfaces is the indication that a fairly large area of conducting phase contacts the solution in the cases of ZnPc and FePc. A rough measure of this area is the capacitive charge injected into the interface in step experiments with an electroinactive medium. We performed a series of such experiments with step magnitudes of 0.3–0.4 V at electrodes immersed in 0.1 M KNO_3. Table I summarizes

the data for Au, ZnPc, and FePc. Shown there are the charges injected in the first 1 ms for Au and in the first 2 ms for the phthalocyanines. A longer time was chosen for the phthalocyanines because these films are more resistive and a slower rise is seen in the charge. In general, Anson plots[45] could not be used to estimate capacitive charge, because the Q-t curves did not follow diffusion-limited behavior after the initial rises. Still, those rises were sharp in all cases, so the estimates of capacity provided in Table I ought to be reliable enough for our purpose, which is to show that the interfacial capacitances for FePc and ZnPc electrodes were comparable to that of the bare gold surface.[51] In contrast, the corresponding capacitances for perylene and polystyrene, coated at 1000–3000 Å thicknesses, were two to three orders of magnitude smaller than at gold.

If the Faradaic activity on the phthalocyanines electrodes really arises through pinholes, then these results must be explained in terms of aggregate exposed gold surfaces totaling 10–50% of the total disk area in the cases of ZnPc and FePc, even while one admits to total coverage of the gold by perylene and polystyrene at the same thickness. Observations by optical microscopy of the phthalocyanine films revealed no defects at all and no evidence of crystallinity. Electron microscopy demonstrated the presence of microcrystals with dimensions of ~100 Å.[52] These observations accord with reports in the literature concerning general features of phthalocyanine deposits,[48] and one could reasonably expect them to reveal any defects that might expose 10–50% of geometric area of the gold underlayer. In contrast, the perylene films show obvious crystallinity under optical examination at 225X. They are far less adherent than the phthalocyanine films and seem much more likely to have pinhole defects. Even so, coverage of the gold by just 1000 Å removes electrochemical activity altogether (see Figure 1) and sharply reduces the interfacial capacitance.

In the face of this evidence and other points cited below, one must favor the idea that facile Faradaic activity in the ZnPc and FePc systems occurs directly on the molecular surfaces. With that hypothesis, the variations in interfacial capacitance would not be interpreted in terms of differences in exposed active area, but instead via differing electrical properties at the interfaces between the various conducting solids and the solution.

Working Ranges. In deaerated 0.1 M KNO_3. ZnPc shows a flat background response from 0.0 V vs. SCE to −0.8 V. Beyond that point there is a small cathodic peak near −0.9 V and a large current rise at the cathodic limit of −1.1 V. Current flow at this limit yields catastrophic failure of the phthalocyanine overlayer. A scan positive from 0.0 V shows a quasi-reversible couple at 0.5–0.8 V and an anodic limit at +1.1 V. This limit is not accompanied by failure of the electrode.

FePc has a narrower working range. The cathodic and anodic limits are −0.75 and +0.5 V, respectively. No voltammetric structure is seen in that interval. The FePc electrodes also fail at the negative limit.

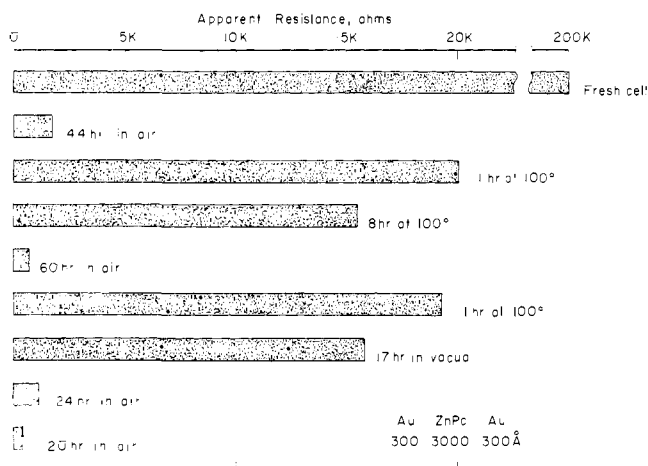The chemical processes responsible for the background

Figure 4. Effects of various treatments on conductivity in an Au/ZnPc/Au sandwich device.

currents are not now understood. It is notable, however, that the narrower limits for FePc correlate with the relative ease of oxidation and reduction of this molecule with respect to ZnPc.[53,54]

Ambient Effects on Solid-State Conductivity. It is known that vacuum-deposited films of the phthalocyanines have the α modification of crystal structure, which can be converted into the β form by heating to temperatures above 300 °C. Earlier studies of α-H_2Pc and α-CuPc have shown that conductivities increase markedly in the presence of oxygen, which apparently enters the crystals as an acceptor impurity.[49,55] In contrast, the conductivities of the β phases are not enhanced by such exposure.[49,55] We have observed similar ambient effects with ZnPc and FePc, and we have found that these effects are mirrored in the electrochemical behavior of electrodes made from these materials.

Figure 4 shows the changes in apparent resistance of an Au/ZnPc/Au sandwich cell after exposures to successive treatments. The apparent resistance is defined here as the ratio of polarizing voltage to current flow when the top electrode is at −1.0 V vs. the bottom one. The resistance is "apparent" because the polarization curves are nonlinear under some circumstances. It nevertheless serves as a guide to conductivity. The fresh cell taken straight from the evaporator was quite resistive, but aging in air and darkness for 44 h produced a reduction in resistance of 100-fold. Baking at 120 °C in air for 1 h caused an increase of one order of magnitude. Further heat treatment brought little change, but reexposure to air for 60 h yielded a sharp drop in resistance. Another baking period elevated the resistance back to the 20K region, and cooling in vacuo essentially maintained the resistance near that level. A final lengthy period of aging in air caused a drop in resistance below the 1K level. It is evident from these experiments that atmospheric constituents control the conductivity of the phthalocyanine layer. They probably gain access through pinholes in the thin metal top layer.

Parallel effects were seen for Au/FePc/Au cells, but the conductivities at all stages were significantly higher than for devices based on ZnPc. Fresh cells containing 3000-Å thicknesses of FePc gave resistances of a few kiloohms, and long-term exposure to the atmosphere dropped the resistance to 100 ohms or less.

Resistance changes of H_2Pc, FePc, and ZnPc sandwiches after 7 days of aging in air are summarized in Table II. Cells involving both α- and β-phase phthalocyanines were tested. The latter were fabricated by annealing the vacuum-deposited α phase at 300 °C in air for about 1 h before depositing the top gold electrode. It is interesting that the resistances of the β

Table II. Apparent Resistances of Phthalocyanine Sandwich Cells

compd[a]	thickness, Å[a]	crystal form	resistance, ohms[b] fresh	aged[c]
H_2Pc	2700	α	1.8×10^8	2×10^3
H_2Pc	2700	β	1×10^7	1.5×10^{10d}
ZnPc	3000	α	$1-4 \times 10^6$	200
ZnPc	3000	β	$1-4 \times 10^6$	1×10^6
FePc	3000	α	several kΩ	100

[a] Sandwiches had gold contacts of 300-Å thickness above and below the molecular layer, which had the thickness shown in the second column. [b] Ratio of polarizing voltage to current flow with top electrode at −1.0 V vs. bottom electrode. [c] 7 days in air. [d] Device was baked at 120 °C in air for a brief period early in the aging process.

Table III. Apparent Resistance Measurements of ZnPc Sandwich Cells[a]

ambient	resistance, ohms[b] fresh	aged[c]
dry N_2	5×10^6	3×10^6
wet N_2	5×10^6	7×10^4
dry air	1×10^6	5×10^3
wet air	1×10^6	2×10^2

[a] ZnPc layer at 3000 Å, Au contacts at 300 Å each. [b] See note b, Table II. [c] 7 days.

phthalocyanines were virtually unchanged by exposure to air. This contrast between the α and β phases accords with earlier observations concerning H_2Pc and CuPc.[49,55] Presumably, it manifests a difference in the abilities of the two crystal structures to accommodate oxygen[49] and water from the atmosphere.

We note that each "fresh" cell suffered an atmospheric exposure of several minutes during its transfer from the evaporator to the locale where the resistances were measured. This exposure, rather than any intrinsic feature of the phthalocyanine layer, determines the initial resistances of the cells studied here.

The possibility that atmospheric water plays a role in reducing resistances in the phthalocyanines appears not to have been recognized in the literature. In order to differentiate the effects of water and oxygen, several Au/ZnPc/Au cells were aged for 1-week periods in four different ambients, as shown in Table III. Dry conditions were obtained by sealing the cells in desiccators containing either high-purity N_2 or air and P_2O_5. Wet N_2 was established in a chamber containing a pool of water at room temperature. Wet air refers to direct atmospheric exposure. Oxygen clearly has a strong effect on resistance, whether moisture is present or not; however, the combination of the two agents was most effective in increasing conductivity. Interestingly, moisture increases conductivity significantly even without long-term exposure to oxygen. This observation may reflect an independent role of absorbed water, or it may indicate a synergistic effect in which the absorbed water enhances conductivity engendered by oxygen absorbed either in the transfer from the evaporator to the sealed chamber or in the transfer from the chamber to the final measuring station. The latter prospects seem more likely because oxygen is probably necessary as the acceptor impurity leading to the formation of holes, which are the majority carriers.[49,56,57] The role of water is less clear. It may act as an axial ligand for the phthalocyanines and thereby enhance the donor strength of a site. Alternatively, it may stabilize a superoxide or oxide site by dipolar effects, or it may convert them to the stable hydroxide form.

The zinc and iron phthalocyanines, when doped by absorption of oxygen and water, are rather well-behaved p-type semiconductors. Ohmic contacts are made with gold, and
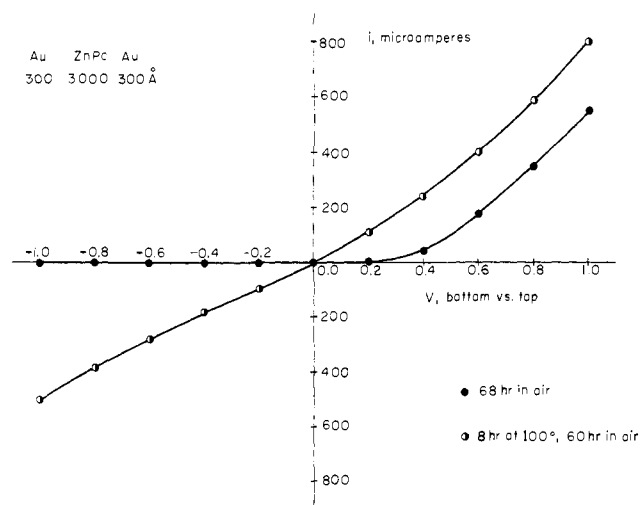
Figure 5. Nonlinear current-voltage characteristics observed for an Au/ZnPc/Au sandwich device.
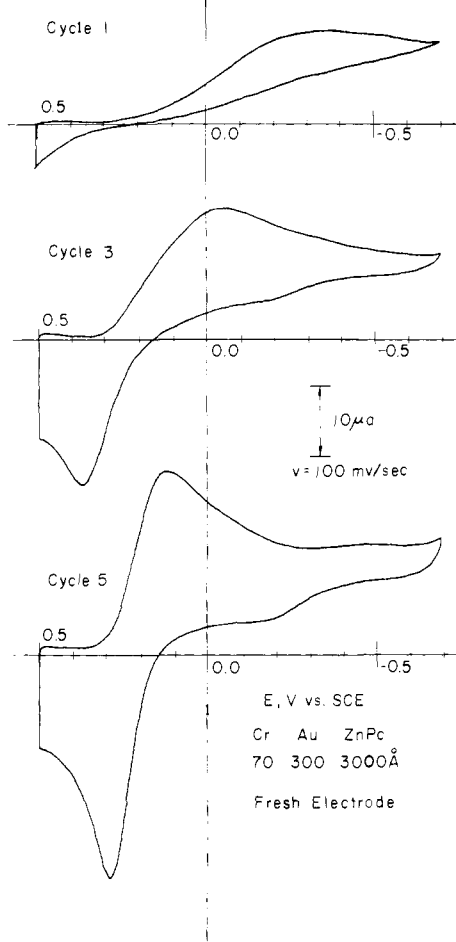

Figure 6. Growth of reversibility at a fresh ZnPc electrode. Solution was 1 mM $Fe(CN)_6^{3-}$ in aerated 0.1 M KNO_3.

Figure 7. Temporal effects on cyclic voltammograms recorded at a ZnPc electrode that had been exposed to air for 24 h beforehand. Solution was 1 mM $Fe(CN)_6^{3-}$ in aerated 0.1 M KNO_3.

Figure 8. Temporal effects on cyclic voltammograms recorded at a fresh FePc electrode. Solution was 1 mM $Fe(CN)_6^{3-}$ in aerated 0.1 M KNO_3.

rectifying junctions are observed with Al and In.[57] The barriers at interfaces with In show characteristics of nearly ideal Schottky junctions.[57]

Figure 5 reveals an interesting aspect of the time course of carrier formation by atmospheric exposure. It is an extreme case in that it exaggerates effects that are generally seen; however, it is instructive as a study. The noteworthy aspect is the diode-like polarization curve that was observed after initial exposure of an Au/ZnPc/Au sandwich to air. Such nonlin-
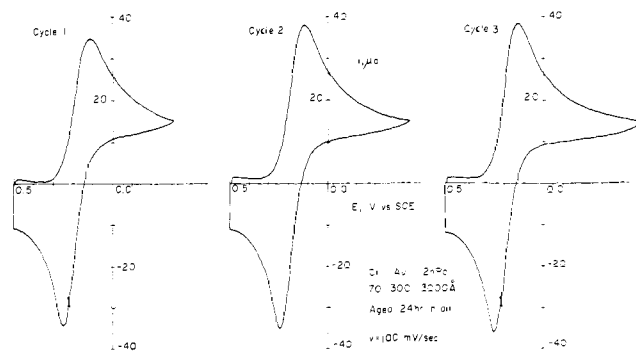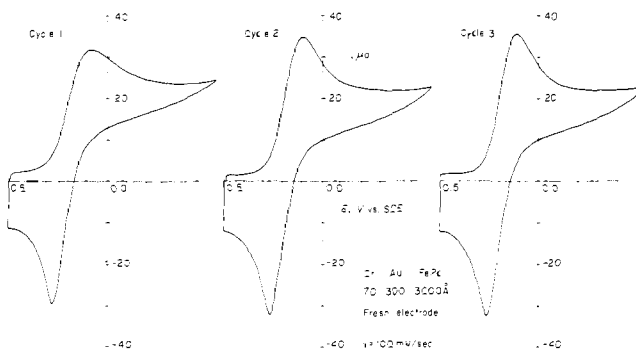
earity is not generally expected in this symmetrical device. It apparently arises because the distribution of carriers is not uniform, but instead favors the region near the top electrode (and the atmospheric interface). Heat treatments and further exposures to air eventually remove the nonlinearity altogether, and a symmetric, ideal polarization curve reflecting high conductivity is achieved. These treatments apparently serve to distribute carriers uniformly within the phthalocyanine.

Environmental Effects on Electrochemistry. The increased conductivities of the phthalocyanine phases upon exposure to oxygen and water are also manifested in their electrochemical responses. Consider the results of Figure 6, which were obtained with a fresh ZnPc electrode. An irreversible voltammogram with low cathodic peak current for ferricyanide reduction was observed in the first cycle, but the responses became more reversible as the measurements were repeated. These cycles were recorded at intervals of 3 min. By the fifth cycle, the response had virtually reached a limiting degree of reversibility. These results indicate that the carrier density within the film increased quickly after the electrode was immersed in the solution. The irreversibility in early cycles may manifest either uncompensated iR losses within the film or sluggish electrode kinetics resulting from low carrier density at the interface.

In contrast, a reversible voltammogram was recorded from ferricyanide solution even on the first cycle when the ZnPc electrode was aged in air for 24 h before use. As Figure 7 shows, subsequent cycles did not yield significant changes in the voltammogram.

The electrochemical response at a fresh FePc electrode was more reversible than at the fresh ZnPc surface. Figure 8 shows that even the initial response was quite good, and only slight improvements were seen in subsequent cycles. These results indicate that the carrier densities in the fresh FePc phases are fairly high, and they generally accord with the differences in
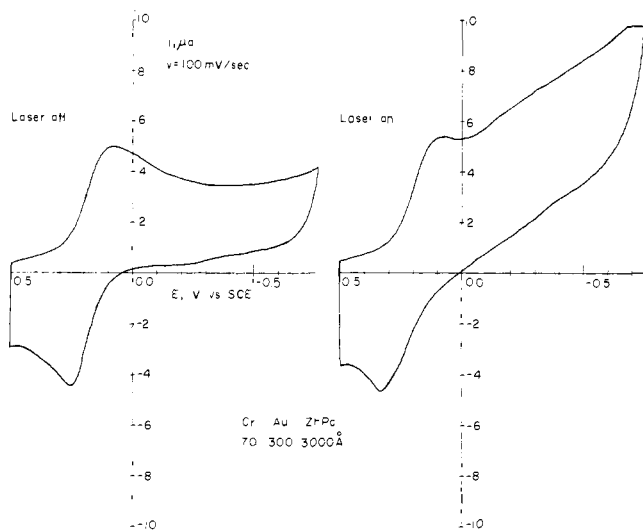
Figure 9. Photoeffect at a ZnPc electrode immersed in aerated solution containing 0.1 mM Fe(CN)$_6{}^{3-}$ and 0.1 M KNO$_3$.

conductivity between fresh FePc and ZnPc sandwich cells.

The time scale of the improvement in conductivity upon immersion of the ZnPc electrodes is much shorter than the corresponding period for enhancement of conductivity in sandwich devices exposed to air. This effect may manifest only the lack of a metal overlayer in the former case, so that oxygen and water have free access to the ZnPc phase. Alternatively, it is conceivable that the presence of water at high concentration facilitates the doping by oxygen dissolved in solution.[58]

Voltammetry of Oxygen Reduction and Other Processes. A marked difference in voltammetric response was observed between gold and ZnPc thin film electrodes when the electrode potential was scanned negatively in an aerated ferricyanide solution. Figure 2 shows the contrast. The gold electrode yields (1) a reversible response for the ferri-/ferrocyanide couple and (2) the familiar irreversible reduction of molecular oxygen. The ZnPc electrode shows good response for ferri-/ferrocyanide, but no response at all for molecular oxygen. Oxygen cannot be reduced on that electrode at any potential short of the cathodic limit at −1.1 V vs. SCE. This point holds regardless of

the presence of ferri- or ferrocyanide. On FePc, oxygen was reduced, but only at very low levels and largely in concert with the background processes yielding the cathodic limit near −0.7 V. The inability of these materials to allow significant reduction of oxygen is particularly striking in view of numerous reports of electrocatalysis of that Faradaic process by the phthalocyanines. The basis for the contrast may lie in the semiconducting nature of these molecular electrodes.

Pertinent to this point are the photoelectrochemical phenomena that can be observed at ZnPc electrodes. For example, Figure 9 shows that a significant cathodic current corresponding to reduction of oxygen was observed when the ZnPc/solution interface was illuminated at normal incidence by a He–Ne laser (6328 Å, >20 mW/cm^2). The enhanced current is clearly due to oxygen, because it does not appear with deaerated solutions.

Similar photoeffects were observed for the reductions of Pb^{2+} and UO$_2{}^{2+}$ at ZnPc. Voltammograms for these reactions at both gold and ZnPc electrodes are shown in Figure 10. The reduction currents are very small without illumination and are noticeably enhanced by the laser. Background voltammograms recorded in the absence of Pb^{2+} or UO$_2{}^{2+}$ revealed extremely small photoeffects; hence the light-induced activity in frames a and b of Figure 10 can be directly ascribed to reactions of those species. The anodic current corresponding to reoxidation of UO$_2{}^+$ is also slightly photosensitive, but that effect is probably a direct result of photoenhancement in the cathodic process that produces the UO$_2{}^+$ immediately beforehand.

A final system of interest involves the EDTA complexes of Fe(II) and Fe(III). See Figure 10c. The ferrous complex can be oxidized and then reduced again in a nearly reversible fashion at the gold electrode. However, the ZnPc surface requires a substantial overpotential for the oxidation, and it cannot efficiently reduce the resulting ferric complex at all. The anodic peak is slightly photosensitive. It increases by about 10% under laser irradiation. Since the initial scan in this case is positive, this photoeffect is a direct one and is not linked to a prior photostimulated reduction.

Most of our results can be interpreted via semiconduction in the phthalocyanines. If they are regarded as p-type materials, then they are not capable of efficient reductions at potentials more negative than the flat-band value, which seems
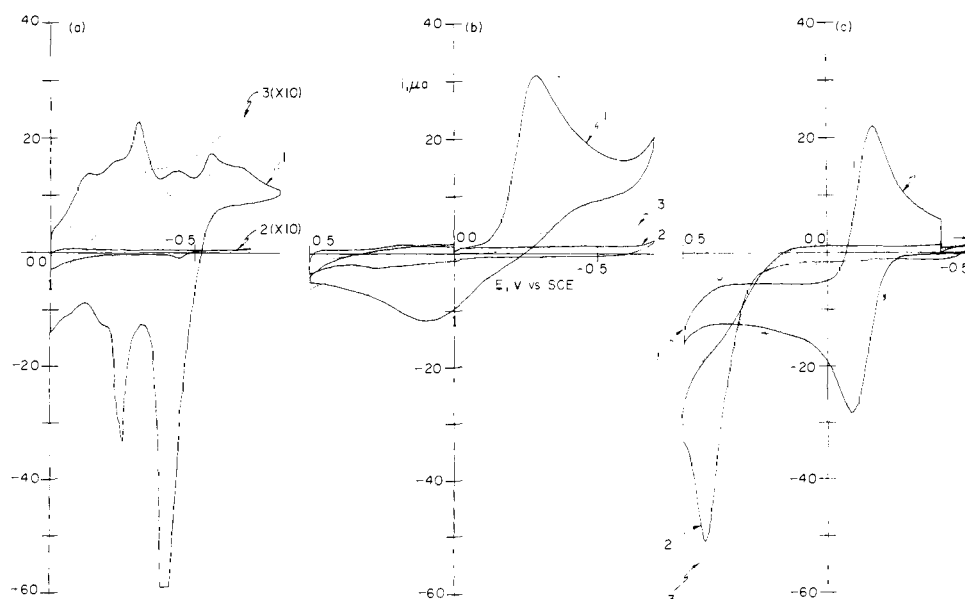
Figure 10. Voltammetric behavior of three other systems: (a) 3.3 × 10^{-4} Pb^{2+} in 0.1 M KNO$_3$. Scans begin at 0.0 V and move negatively at 100 mV/s. (b) 1 mM UO$_2{}^{2+}$ in 0.1 M KNO$_3$. Scans begin at 0.0 V and move negatively. (c) 1.1 mM Fe^{2+} and 1.1 mM EDTA in 0.1 M KNO$_3$. Scan directions as shown. All solutions were deaerated. Curves 1 were for 300 Å Au on 70 Å Cr. Curves 2 were for 3000 Å ZnPc over 300 Å Au on 70 Å Cr, in the dark. Curves 3 were for the ZnPc electrode under illumination at 6328 Å.

to lie near 0 V vs. SCE with these solids.[59-61] At positive potentials, holes are available at the solution interface, and Faradaic processes can be relatively facile. This situation apparently applies for the ferri-/ferrocyanide interconversion, the oxidation of the ferrous–EDTA complex, and the reversible deposition of copper, which occurs quite smoothly on the phthalocyanines. At negative potentials the electronic bands bend downward toward the interface, and the hole population there is depleted. Faradaic reactions are carrier limited and occur only at low rates. The reductions of molecular oxygen, UO_2^+, Pb^{+2}, and the ferric–EDTA complex are all apparently eliminated by this effect. Even the oxidation of the ferrous–EDTA complex, which normally would occur in the negative region, is inhibited. It takes place only when the potential moves into the positive region: thus the overpotential for that process can be interpreted straightforwardly in terms of the potential-dependent carrier density in the interfacial zone.

The photoeffects generally support this interpretation, because the inhibited reductions can all be driven by light. In a simple semiconductor, light can register effects only in a depletion region, because only there does light absorption enhance the carrier density significantly.[59-61] In a p-type material, photocurrents should be generally seen for processes taking place at potentials more negative than the flat-band value. In the case of oxygen at ZnPc, the cathodic photocurrent starts to flow at ~0.1 V vs. SCE, and it increases toward negative potentials.[62] That positive limit should be a fairly good estimate of the flat-band condition for ZnPc.

The photoeffect on the oxidation of the ferrous–EDTA complex is a puzzling result and does not fit neatly into the picture that we have drawn here. It might be accommodated by invoking a light-stimulated population of mediating surface states. It could also manifest only a lowered electrode resistance from heating by irradiation.

Another interesting aspect is the lack of any significant photoeffect at FePc electrodes. This feature might be understood within our hypothetical structure by recognizing FePc as a highly doped p-type material. Thus the depletion layer in the negative potential region would be quite thin, and not much light would be absorbed within it. A second possibility is that FePc contains a large number of intermediate levels that act as recombination centers.

We advance the idea that ZnPc and FePc are reasonably well behaved semiconductor electrodes, because it enables an understanding of nearly all of our observations, and because it provides a framework for additional, more quantitative electrochemical studies at phthalocyanine surfaces. The alternative is that chemical interactions at the phthalocyanines cause selective electrode responses. This idea must have some truth, and it may be important to certain observations reported here, e.g., in determining the overpotential for oxidation of the ferrous–EDTA complex. However, we are unable to build a working model that provides a detailed rationale for our various observations on the basis of chemical selectivity. The semiconductor model succeeds rather well in this regard, and it should be useful for focusing future experimentation.

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