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THE COMBINATION OF PHTHALOCYANINES AND POLYMERS FOR ELECTROCHEMICALLY OR PHOTOELECTROCHEMICALLY INDUCED PROCESSES

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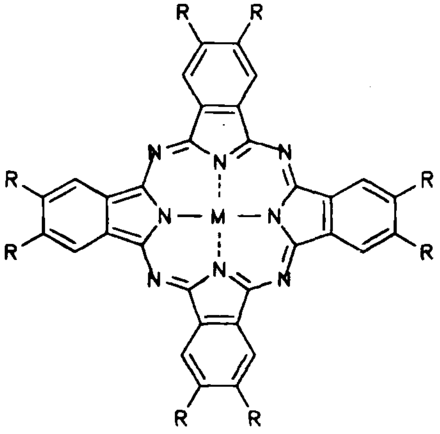
ABSTRACT

Phthalocyanines *1-3* were used in combinations with polymers in order to investigate reduction/reoxidation of thin film electrodes, photoinduced reduction of dioxygen at the junction of thin film electrodes to an electrolyte, and dioxygen reduction in the dark (fuel cell reaction) at dispersions of phthalocyanines on carbon supports. Electrochromic reduction/reoxidation of phthalocyanines also occurs readily inside a polymer matrix if intermolecular particle contact exists. A significant photoreduction of dioxygen is observed if O_2 can form trapped states inside of the bulk of the film, with the result of enhanced photoconductivity. The kind of polymer is of striking influence. Phthalocyanines with central metals forming localized ionized states with dioxygen are active electrocatalysts for dioxygen reduction in the dark if they are finely dispersed on a

carrier. The influence of both phthalocyanine and polymer component in each of the three-mentioned processes is discussed.

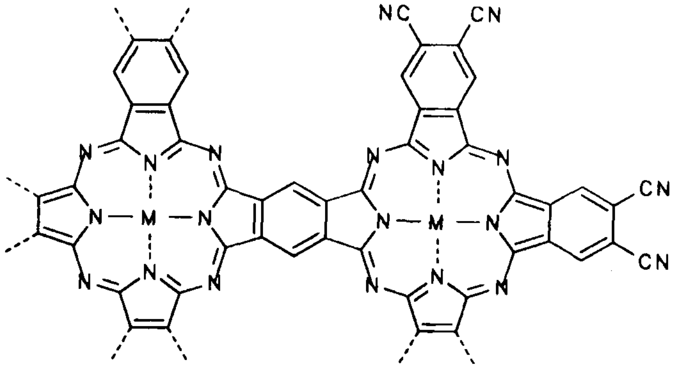
INTRODUCTION

Macrocyclic tetrapyrroles (porphyrins) like phthalocyanines *1* [1-7] are interesting as active materials in various processes of energy conversion and electrooptics. The properties include charge carrier generation and their separation after irradiation with visible light in the solid state in photovoltaic cells [1, 6, 8-13], photoelectrochemical cells [1, 3, 5, 14-21] (conversion of light energy into electrical energy), and electron transfer reactions in the dissolved state in photoredox processes [1, 3, 5, 22, 33] (conversion of visible light into chemical energy). Furthermore, the dioxygen reduction in fuel cells using porphyrins as electrocatalysts is a well-known process for the conversion of chemical energy into electrical energy [1-5, 24-29]. Charge storage processes based on the multi-electrochromic redox behavior of phthalocyanines is another important property [3, 4, 30-36].



1 (R=–H)

2 (R=–C≡N)



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The combination of porphyrines with polymers is a powerful tool in designing new materials with special properties. Preparative macromolecular chemistry opens the way for synthesizing various combinations [1, 3]:

Type A polymers: The ligand is part of a polymer network or polymer chain (e.g., polymeric phthalocyanines).

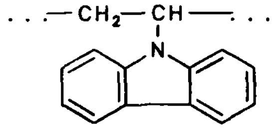
Type B polymers: The metal atom of a chelate is part of a polymer chain (e.g., one-dimensional polymeric stacked phthalocyanines).

Type C polymers: Chelates are covalently bound across the ligand to a polymer chain (e.g., covalently bound polymeric phthalocyanines).

Type D polymers: The interaction occurs coordinatively at the metal atom of a chelate with polymer donor ligand or electrostatically between a charged phthalocyanine and a charged polymer chain.

Type E polymers: The simplest combination treats the physical incorporation of phthalocyanines into the matrix of an organic (or inorganic) polymer.

Various examples of Type C polymers were presented at the Macromolecule-Metal Complexes Conference II (MMCII) held in Tokyo (October 14–17, 1987). The results were published elsewhere [23]. The present paper for MMCIII, held in Lawrenceville, New Jersey (July 23–28, 1989) describes some of our recent results on solid devices consisting of Type A and mainly Type E polymers. The reactions investigated are redox behavior of thin film electrodes, photoelectrochemistry with redox couples in solution, and electrocatalytic dioxygen reduction at phthalocyanines on carbon substrates.



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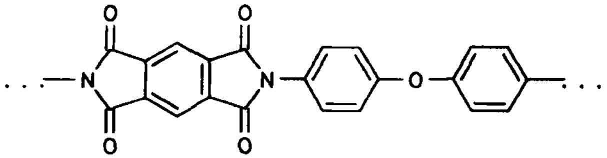

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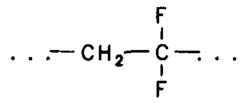


$$\cdots-CH_2-\underset{F}{\overset{F}{C}}-\cdots$$

6

CHARGE/DISCHARGE BEHAVIOR OF PHTHALOCYANINE THIN FILM ELECTRODES

The π-electron-rich phthalocyanines can be reduced or oxidized either in solution or as thin films [1, 2, 6]. From our previous investigations [30, 31] it is known that thin films of unsubstituted *1* and of *1* containing electron-donating substituents in contact with 1 *N* acidic solution cannot be reduced in the employed potential range of +900 to −300 mV vs NHE. The limit is the beginning of hydrogen formation in the cathodic region. However, the reduction potential of phthalocyanine thin film electrodes is shifted in the anodic direction depending on the electron-attracting properties of substituents at the ligand [30, 31, 35]. Compound *2* (M = 2H) containing electron-attracting cyano groups is reversibly reduced/reoxidized at ~ +200 mV vs NHE in contact with 1 *N* acidic solution. Compound *2* (M = 2H) was embedded in polymers with the goal of enhancing the mechanical stability and flexibility of the films and maintaining the outstanding electrochemical properties at the same time. In addition the influence of the polymer environment should be studied.

Intensely green-colored and smooth films of *2* (M = 2H) [37] in poly(*N*-vinylcarbazole) *4* and poly(4,4′-oxydiphenylenepyromellitimide) *5* were prepared by casting from DMA solutions on gold substrates [35]. The films with a thickness of ~300 nm contain *2* and *4* or *5* in a 1 : 1 ratio by weight. In addition, *2* in poly(vinylidenefluoride) *6* was obtained analogously. The transmission VIS spectra give information about the chemical environment of *2* inside the polymers (Fig. 1, Curve a). In solution (DMF) the spectrum of *2* is characterized by Q-band absorptions at λ = 642 and 692 nm [6, 37], whereas in the solid state a broader absorption at λ = 655 nm [35] is typically due to dipole-dipole exciton splitting of the main singlet transition by intermolecular interactions [6]. Comparing these results with our previous study [35], it can be seen that solid particles of *2* exist within the polymer matrix, and that the amount of dissolved *2* within the polymer increases as follows: $6 < 4 < 5$.

The electrochemical behavior of the films in contact with 1 *N* aqueous acid was investigated by cyclic voltammetry. As reported previously [30], *2* (M = 2H) exhibits reduction at 230 and 205 mV and oxidation at 282 and 187 mV vs NHE (Table 1) with high reversibility and electrochemical stability. The charge under the curve corresponds to around 3 F/mol. The reversible reduction takes place through incorporation of electrons from the gold carrier and charge compensating protons from solution (Eq. 1). *2* (M = Zn, Cu) behaves similarly [30], and therefore further results will not be described here.

$$Pc(CN)_8 + nH^+ + ne^- \rightleftarrows Pc(CN)_8^{n-}H_n^+ \qquad (n < 3) \qquad (1)$$

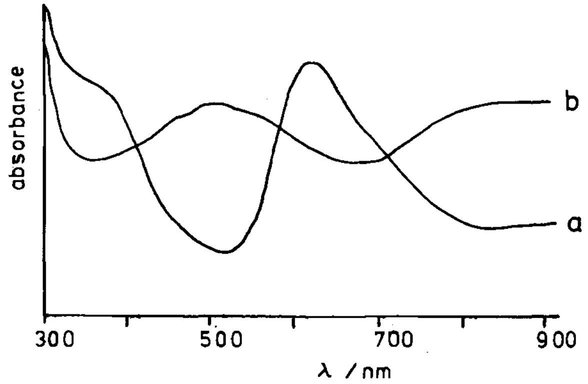


FIG. 1. UV/VIS spectra of *2* (M = 2H) interior of the matrix of polyvinylidenefluoride *6* (1 : 1 by weight) on ITO (thickness: ∿250 nm). Electrolyte: 1 *N* aqueous HCl. (a) Original layer. (b) Reduced at −120 mV vs NHE.

TABLE 1. Peak Potentials of Stable Cycles for the Reduction and Reoxidation of Films from *2* and *3* in 1 *N* Aqueous Acidic Solution. Scan Rate: 40 mV/s

Film composition *2, 3*	Polymer *4-6*	Peak potentials in mV vs NHE				Charge storage, F/mol
		E^{I}_{red}	E^{I}_{ox}	E^{II}_{red}	E^{II}_{ox}	
2 (M = 2H) [30][a]	–	230	282	205	187	2.7
2 (M = 2H)[a]	*4*	210	287	202	205	2.5
2 (M = 2H)[a]	*5*	202	305	95	205	1.9
2 (M = 2H)[b]	*6*	287	305	208	217	2.4
2 (M = Cu) [30][b]	–	163	195			2.7
3 (M = Cu) [33][b]	–	195	90			1.0

[a] Electrolyte: 0.5 *M* H_2SO_4.
[b] Electrolyte: 1 *M* HCl.

Electrodes coated with films of mixtures of *2* and the polymers show similar cyclic voltammograms. The cyclic voltammogram of *2* in poly(vinylidenefluoride) is shown in Fig. 2. In the course of the redox cycle an electrochromic color change is observed reversibly over several cycles from green to red during reduction (Fig. 1, Curve b). For *2* in *4* or *6* (1 : 1 by weight), the charge exchanged in either branch of the voltammograms is stable after the second cycle and corresponds to the charge of a pure film of *2* (Table 1).

A linear relationship exists between the cathodic and the anodic peak currents and scan rate in the range of 20 to 400 mV/s, indicating Nernstian behavior without the mass transfer limitation of charge compensating protons. In contrast, films of *2* in polymer *5* show broadening of the peaks in the voltammogram and a cathodic shift of E_{red}. The charge exchanged during the cycles decreases (Table 1), and a deviation from the linear relationship of the peak current with the scan rate is observed (diffusion-controlled intercalation of charge-compensating protons).

According to VIS spectra, *2* in *5* is partially molecularly dissolved [35]. This leads to a lower amount of exchanged charge during the electrochemical redox process in comparison to *2* in *4* or *6*. Therefore a phthalocyanine intermolecular particle contact is necessary to realize an electrochemical redox process. The influence of the polymer matrix on the

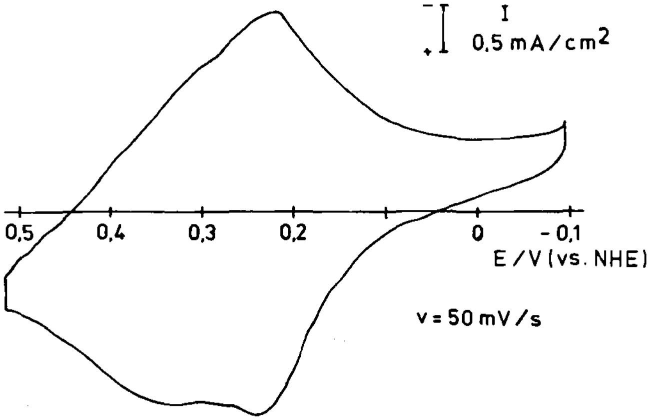


FIG. 2. Cyclic voltammogram at 50 mV/s of *2* (M = 2H) in poly(vinylidenefluoride) *6* (1 : 1 by weight) in contact with 1 *M* HCl (thickness: ∿250 nm).

phthalocyanine crystallization process is important for the electrochemical performance of the thin films. This is discussed in detail in the next section. The polymers *4* and *6* are more easily swelled in comparison to the polyamic acid precursor of *5* in DMA [35], thus resulting in good crystallization of *2* as analogously reported for substituted vanadyl phthalocyanine in vinyl chloride/vinyl acetate copolymer [38]. The polarity of the polymer seems to have no predominant influence on the electrochemical redox behavior of the thin film electrodes. Polymer *6* with a very high dipole moment of 2,1 D does not exhibit enhanced redox behavior for *2* in comparison to polymer *3*.

Thin films of the polymeric phthalocyanine *3* (M = Cu) were investigated previously [33]. Thin film electrodes were prepared by the reaction of 1,2,4,5-tetracyanobenzene on basal plane graphite covered with a thin copper film. The VIS spectra is similar to that of *2* (M = Cu) [33]. Polymer *3* (M = Cu) exhibits a cyclic voltammogram with peak potentials similar to *2* (M = Cu) [30, 33], but the charge under the curve (after subtraction of a high double layer capacity for the polymer film *3*) corresponds to only one electron per monomer unit in the polymer for the cathodic as well as for the anodic branch of the cycles. This may be due to the presence of polymeric phthalocyanines with different degrees of annealing of the phthalocyanine units, resulting in redox states at different potentials hidden under the high double layer capacity.

LIGHT-INDUCED DIOXYGEN REDUCTION AT PHTHALOCYANINE THIN FILM ELECTRODES

In photoelectrochemical cells the interface between the semiconductor phthalocyanine and an electrolyte containing a redox couple forms a junction which is active in photoconversion. Photoreduction occurs at the interface of the bulk and the solution, which is representative of the p-type character of the phthalocyanine. Various redox couples in aqueous solution were intensively investigated by using phthalocyanine thin films obtained by vapor deposition or by drop or spin coating processes [1, 3, 5, 14–21]. In this section we describe the photoreduction of dioxygen at a *1* (M = Zn) thin film electrode on ITO by illumination with visible light.

Thin films of *1* (M = Zn) within a polymer matrix (1 : 1 by weight) were prepared by a drop coating technique. This process produces smooth homogeneously colored films (thickness ~250 nm, roughness ~40 nm). In addition, vapor deposited films (thickness 50 nm) were prepared.

The photoelectrochemical measurements during front side illumination through the electrolyte were conducted in 0.5 *M* KNO_3 (pH 5) at a dioxygen concentration of 1.3×10^{-3} mol/L, corresponding to a pure O_2 atmosphere (760 torr) at room temperature. Figure 3 contains the cyclic voltammograms of the zinc complex *1* electrode obtained by vapor deposition and casting in poly(vinylidenefluoride). For both electrodes the most efficient layer thickness is chosen. The cathodic photocurrents increase up to a layer thickness of 250 nm for cast films and 50 nm for vapor-deposited films. Higher layer thicknesses did not lead to enhanced photocurrent. When the electrode potential is scanned negatively in the dark in the presence of O_2, no cathodic current corresponding to reduction of dioxygen is observed. The same situation is evident when the electrode is scanned negatively under an inert gas (argon) in the dark and also under illumination. Only under light in the presence of dioxygen does a significant irreversible oxygen reduction occur. At −120 mV vs NHE, a cathodic photocurrent density as high as 0.1 mA/cm² was observed for cast films of *1* in the polymer *6*. The current density of cast films using polymers other than *6* and of vapor deposited films of *1* is lower (Fig. 3, Table 2). The process is highly specific for dioxygen. Other acceptors, e.g., potassium ferricyanide and *p*-benzoquinone employed in concentrations of 10^{-3} mol/L (like O_2 concentration in solution), show only small differences between the cathodic current in the dark and under illumination [39]. Table 2 compares the results of current densities at

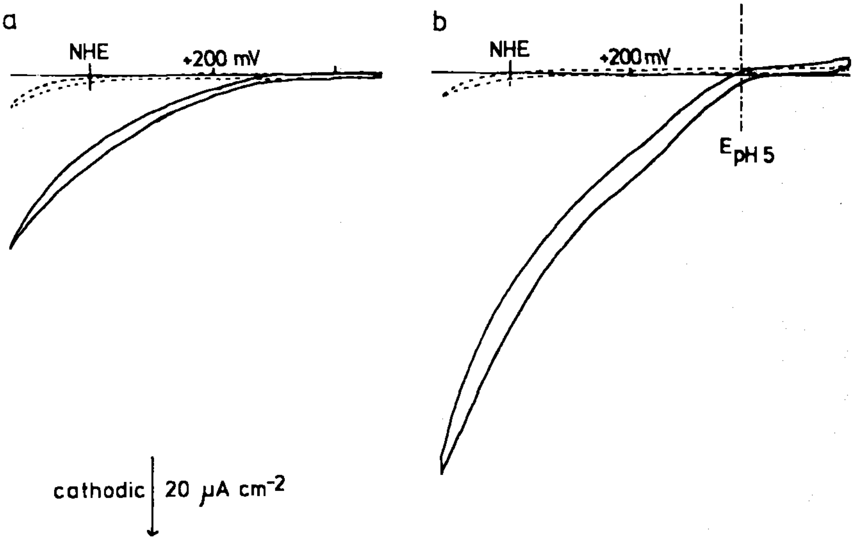


FIG. 3. Cyclic voltammograms at 20 mV/s in aqueous 0.5 *M* KNO_3 (- -: in the dark; —: under illumination with 400 mW/cm^2). (a) Vapor deposited 50 nm thin film of *1* (M = Zn). (b) Drop cast 250 nm film of *1* (M = Zn) in poly(vinyldenefluoride) *6* (1 : 1 by weight). Measurements in a saturated solution of dioxygen (1.3 × 10^{-3} mol/L).

− 120 mV vs NHE for *1* (M = Zn) in various polymers. Comparison of the photoelectrochemical activities shows the general trend that polyvinyl compounds containing polar substituents are advantageous. The poly(vinylidenefluoride) film leads to the highest photocurrents and the best values of the ratio of the currents under illumination and in the dark. The high dark current of *2* (M = Zn) [3] cannot be altered by illumination (Table 2). The same result was obtained when employing the highly conducting polymeric phthalocyanine *3*. On the one hand, the cyano groups lead to more n-type conducting behavior in phthalocyanines, and on the other hand, the conductivity of highly conducting organic solids is less altered by illumination.

Figure 4 shows that the films consisting of different amounts of *1* (M = Zn) in *6* give the highest activity of the photocurrent density at a weight ratio of the components between 0.5 and 1. Better intermolecular contact of the complex leads to increased electronic conductivity in bulk. In addition, the polymer plays an active part in photocatalytic activity. More details of the process and an intensive discussion, including the

TABLE 2. Dioxygen Reduction by Various Electrodes of *1*, *2* (M = Zn). Measurements in 0.5 *M* KNO_3. Current Densities during Cyclic Voltammetry at an Electrode Potential of − 120 mV vs NHE

		Current density, $\mu A/cm^2$		
Chelate	Polymer	Dark (i_D)	Irradiation (i_I)	i_I/i_D
1[a]	–	10	46	4.6
2[b]	–	300	350	1.2
1[c]	PVPy	5	7	1.4
1[c]	PS	5	12	2.4
1[c]	Nafion	9	30	3.3
1[c]	PAN	4	14	3.5
1[c]	PVC	4	25	6.3
1[c]	PVC_Z	5	35	7.0
1[c]	6	6	100	16.7
2	6	300	350	1.2
1[d]	6	240	240	1

[a] Vapor deposited film, 50 nm thickness.

[b] Cast film, 130 nm thickness.

[c] Cast films in mixture with polymers (1 : 1 by weight), thickness 250 nm.

[d] *1* with M = Fe or Co.

dependence of the photocurrent on the light intensity, the dioxygen concentration, and the layer thickness, will be published elsewhere [39]. It will be shown that the conversion efficiency at 622.5 nm is ~2%.

The influence of the polymer environment on photoelectrochemical behavior is significant (Table 2). The cast films show significant differences in the VIS spectra. Layers of vapor-deposited phthalocyanines can consist of different polycrystalline structures with different electronic spectra due to different Davydov splitting. The α- and β-modifications, both characterized by a slip stack orientation of adjacent phthalocyanine rings [6], give two distinguishable absorptions in the visible region showing different intensities for each polymorph [1, 2, 40–42]. The vapor-deposited films show the absorption bands of the α-modification at 620 nm (higher intensity) and 690 nm [42]. The decreasing intermolecular overlap in the β-polymorph shifts the bands toward longer wavelengths

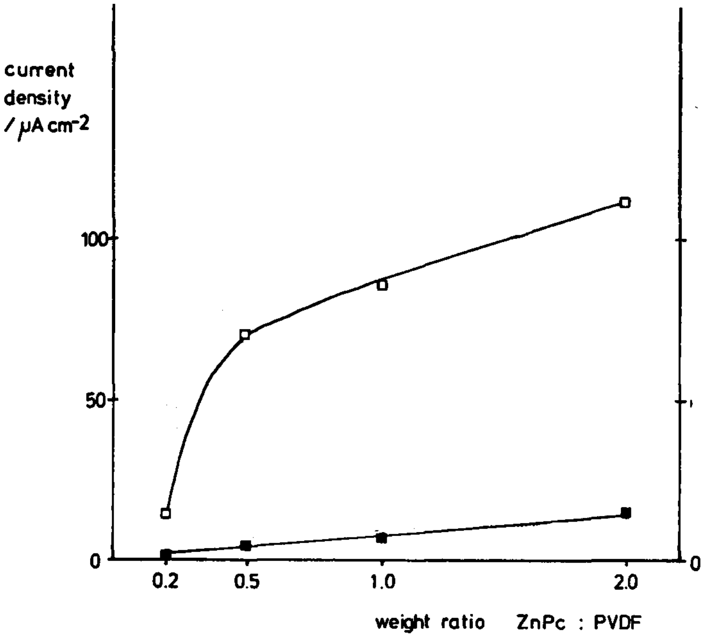


FIG. 4. Stationary cathodic currents for dioxygen reduction (electrode potential -60 mV vs NHE) are dependent on the concentration of *1* (M = Zn) in poly(vinylidenefluoride). Measurement in 0.5 *M* KNO_3 (■: dark current activity; □: current activity under illumination with 400 mW/cm^2).

with the band at the longer wavelength now being of higher intensity [41, 42]. The β-polymorph is the thermodynamically stable modification which shows low electronic conductivity but higher photoconductivity [43]. Within the matrix of poly(vinylidenefluoride) *6*, the phthalocyanine seems to exist in the β-modification (Fig. 5). With increasing polarity of the polymer, the portion of β-modification increases and the α-modification decreases (Fig. 5). This tendency runs parallel to an enhanced cathodic photocurrent (Table 2). The low activity in the presence of poly(2-vinylpyridine) may be due to the extremely high Lewis basicity of the polymer which results in the strong donor ability of the pyridine to the zinc central metal. This seems to have a strong influence on the phthalocyanine p-semiconducting properties. Poly(vinylidenefluoride) produces a high cathodic photocurrent. For this polymer it is reported [11] that due to a large dipole moment of 2.1 D, a sizable electric field of 10^6 V/cm in the microenvironment of a monomer unit is produced. This could en-

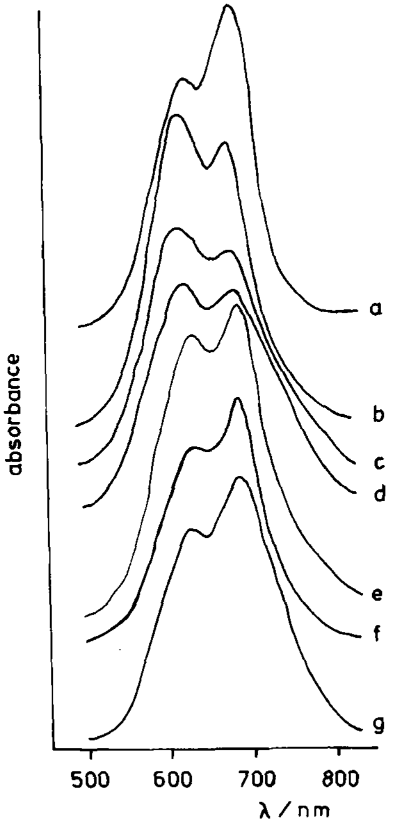


FIG. 5. Visible absorbance spectra of *1* (M = Zn) in various polymers (1 : 1 by weight): (a) PVPy, (b) PS, (c) Nafion, (d) PAN, (e) PVC, (f) PVCz, (g) PVDF.

hance electron-hole dissociation and transport compared to the recombination and thus contribute to an increase of the photocurrent.

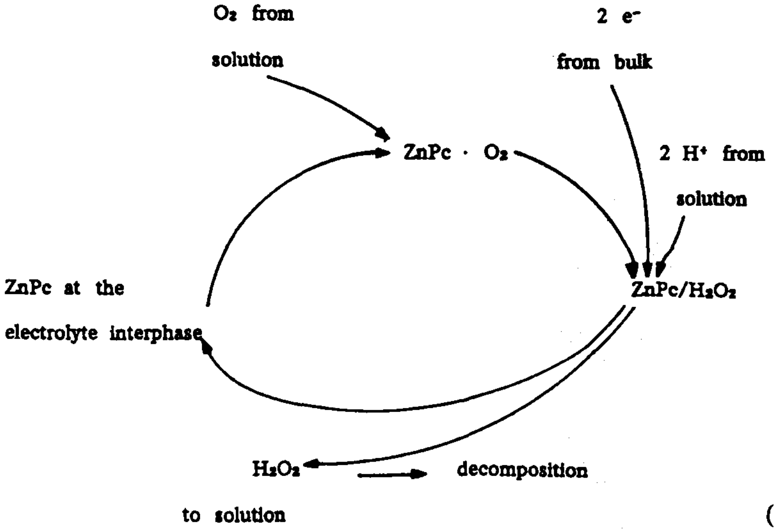
As mentioned before, unsubstituted phthalocyanines behave as p-type materials with a high acceptor concentration. The acceptor dioxygen is the most important dopant incorporated into the phthalocyanine bulk or film [6, 14–16]. The presence of these defect sites is a fundamental prerequisite for the good performance of phthalocyanines in photovoltaic cells and for their electrical conductivity and photoconductivity. The defect density is as high as ~10^{18} cm^{-3}, and the states are located ~0.4 eV below the conduction band edge (width of the forbidden band gap: ~2 eV). The β-modification which is formed in polar polymers provides a 10-times higher density of electron traps and a 5-times higher charge carrier mobility compared to the α-modification. Irradiation results in a $S \rightarrow S_1$ transition and the formation of MPc* with an energy of around 1.8 eV [6]. The energy between the singlet state and, after electron transfer, the ionized intermediate $MPc^{+\cdot}/O_2^{-\cdot}$ is ~0.2 eV. Therefore, after illumination, an energy of only 0.4 eV is needed for the generation of free charge carriers. This energy is found to be the thermal activation energy of the photocurrent over a wide temperature range (30 to 200°C) [6]:

$$\mathrm{MPc/O_2} \xrightarrow[\substack{S_0 \rightarrow S_1 \\ (\sim 1.8\ \mathrm{eV})}]{h\nu} \mathrm{MPc^*/O_2} \longrightarrow$$

$$\mathrm{MPc^{+\cdot}/O_2} \xrightarrow[(\sim 0.4\ \mathrm{eV})]{\Delta T} \text{free charge carriers} \qquad (2)$$

Charge carrier photogeneration and transport of charges depend on the magnitude of the applied electrical field and the internal field of 10^6 V/cm induced by the poly(vinylidenefluoride) in the immediate neighborhood of repeating monomer units [11]. Therefore, polar polymers have two effects: formation of the favorable β-polymorph and enhanced photoconductivity.

The reduction of dioxygen dissolved in the aqueous phase occurs at the semiconductor electrolyte junction and not in the interior of the bulk film. For single crystals of phthalocyanines, the diffusion constant (at 242°C) is 7×10^{-9} cm²/s [44]. That means O_2 diffuses only 50 nm in 1 h. For fluorinated polyalkenes the permeability constants of O_2 are also low [45]. Our results of a high cathodic photocurrent rising immediately with illumination (constant value after less than 1 ms) [39] shows that the enhanced photoconductivity produces charge carriers for the reduction of O_2 at the junction. The selectivity toward dioxygen (in solution) can be explained by taking into account the nature of the surface states on the molecular scale [39]. In addition, the well-known coordination of O_2 at the metal of the phthalocyanine is responsible for the high selectivity. Therefore, it is reasonable to assume that the kinetics of adsorption, charge transfer, and product desorption differ markedly between O_2 and other acceptors. H_2O_2 is found to be a reduction product; it was detected by the discoloration of aqueous $KMnO_4$ solution and by a specific reaction with titanylsulfate. In a subsequent step, H_2O_2 is decomposed to water. The value of $E(O_2/H_2O_2)$ is +390 mV vs NHE at pH 5, which is close to the flat band potential of the phthalocyanine [6, 18]. The reactions at the junction are simply described as shown in



(3)

ELECTROCATALYTIC DIOXYGEN REDUCTION

Cast films of *1* (M = Fe, Co), prepared as described in the preceding section, exhibit no cathodic photocurrents in the presence of oxygen-saturated electrolytes (Table 2). The Fe(II) and Co(II) complexes are easily oxidized, and they can form localized ionized states in the bulk of the film [6]. These states reduce the mobility of the charge carriers by acting as trapping states. Therefore—as described for single crystals—the photoconductivity is depressed [6, 46]. However, the Fe, Co chelates are active electrocatalysts for dioxygen reduction in fuel cell reactions in the dark [1–5, 24–29]. To enhance their electrocatalytic activity, these complexes were finely dispersed on active carbon in order to have contact of the ionized state with the electrolyte and to realize a high surface area for the interaction between the metal of the chelate and the dioxygen in solution. In addition, the activity is enhanced by heat treatment of the catalysts at 500–900°C in an inert atmosphere [29]. Low molecular weight *1* (M = Fe) and polymeric *3* (M = Fe) were prepared on a high area RB-carbon support by the reaction of Fe(II)-loaded carriers with 1,2-dicyanobenzene and 1,2,4,5-tetracyanobenzene, respectively, in a closed bomb vessel. The formation of the phthalocyanine was confirmed by IR spectroscopy. The carriers contain ~ 10 by weight of *1* or *3*. The samples were pyrolyzed at 800°C for 2 h under argon [29]. For electrocatalytic measurements the catalysts were dispersed in 1 *M* KOH and stirred at 500 rpm. A gold/platinum mesh was used as the working electrode. The results of the electrocatalytic measurements show that polymer *3* (M = Fe) exhibits a higher activity than the low molecular weight *1* (M = Fe), in both the nonpyrolyzed and pyrolyzed states (Table 3). This may be because the high electronic conductivity of the polymers induces the reduction of dioxygen [3]. Equation (4) shows a simple interaction with O_2. The detailed mechanism for O_2 reduction following the peroxide pathway is discussed elsewhere [24].

$$\begin{gathered}\text{Fe(II)-phthalocyanine} \xrightarrow{O_2} O_2^- \cdots \text{Fe(III)-phthalocyanine} \\ \text{(ionized localized states)} \\ \xrightarrow[+\,H_2O,\ -OH^-]{+\,e^-} HO_2^{-\cdot} + \text{Fe(II)-phthalocyanine} \end{gathered} \tag{4}$$

CONCLUSION

The electrochromic reduction and reoxidation of suitable low molecular weight or polymeric phthalocyanines like *2* and *3*, each containing

TABLE 3. Activity of Phthalocyanine Fe-Complexes for the Reduction of Dioxygen at 25°C. Electrolyte: 1 *M* KOH

Chelate	Rest potential vs NHE	Current in mA at various potentials vs NHE		
		800 mV	700 mV	600 mV
1 (not pyrolyzed)	900	5	8	24
1 (pyrolyzed)	900	5	44	76
3 (not pyrolyzed)	900	6	17	41
3 (pyrolyzed)	940	13	53	79

electron-withdrawing groups, can occur readily. Such a material can exhibit real Nernstian behavior even after embedding *2* into polymers if an intermolecular contact of the electrochemically active particles is realized. The polarity of the polymer has no significant influence on the redox behavior of the film, but the mechanical stability and flexibility is improved, which alters the usefulness of the films in electrochromic displays. Films of *4* (thickness >5 μm) containing the phthalocyanines can be drawn from the substrate.

Compounds *2* and *3* exhibit no significant photoeffect, e.g., photoconductivity by illumination with visible light. Therefore, no photoelectrochemical reduction of dioxygen which is present in the electrolyte occurs. Cathodic currents in the dark and under illumination are very similar due to a comparatively high dark conductivity. For the investigation of the photoreduction of dioxygen, photoconducting phthalocyanines like *1* (M = Zn) are used. A very significant photoreduction is measured. On the one hand, "permanent" dioxygen dopes the bulk of the phthalocyanines. The doping results in intermediate states within the forbidden gap of the semiconductor and therefore leads to an enhanced photoconductivity of the solid. On the other hand, "free" dioxygen in the electrolyte can be reduced and significantly enhanced by illumination at the junction of the semiconductor and the electrolyte. A very high cathodic photocurrent is observed. This photocurrent increases if the phthalocyanine is dispersed under continuous particle contact in a polymer matrix. Casting with polymer can lead to a favorable polymorph of the phthalocyanine, and, in addition, the polar poly(vinylidenefluoride) *6* actively enhances the photoconductivity of the film, leading to interesting sensor properties. It is possible to draw off films of *1* in *6* (thickness >5 μm) from the substrate. The influence of substituents on the phthalocyanine ring and the kind of metal ion inside the core is discussed in another paper [39].

Phthalocyanines containing metals like Fe and Co, which can easily change their oxidation state at the central metal, form localized ionized states by interaction with "permanent" dioxygen in the interior of the bulk semiconductor. At the surface of these phthalocyanines the dark reduction of "free" dioxygen results in high current densities. Therefore no photoeffects at the junction of the semiconductor/electrolyte can be seen because the electrical conductivity of the material is not altered significantly by illumination due to localized trapping states. The diffusion constant of O_2 in the interior of the bulk is low. Therefore the efficiency is much higher if the Fe-containing phthalocyanines are finely dispersed on a carrier with a high surface area simply because localized, ionized states are in contact with the oxygen-containing electrolyte. This results in a reduction of O_2 which might become interesting for fuel cell applications.

It was shown that combinations of phthalocyanines and polymers lead to interesting solid structures which are of higher efficiency than the pure compounds. Depending on the desired properties, various compositions were optimized by the appropriate choice of components and procedures to get quite satisfying results in electrochemical, photoelectrochemical, and electrooptical research.

EXPERIMENTAL

Materials

Phthalocyanines *1* were purchased commercially. 2,3,9,10,16,17,23, 24-Octacyanophthalocyanines *2* were prepared as described [37]. Nafion (5 wt% solution; Aldrich), polyacrylonitrile (PAN; Bayer), polystyrene (PS; Aldrich), poly(1-vinylcarbazole) *4* (PVCz; Janssen), polyvinyl chloride (PVC; Janssen), poly(vinylidenefluoride) *6* (PVDF; Aldrich), and poly(2-vinylpyridine) (PVP; Aldrich) were used as obtained. Water for electrolyte preparation was doubly distilled. All salts, acids, gases, and solvents used for the measurements were of analytical grade. RB-carbon support (surface area 1000–1300 m²/g) was obtained from Calgon Corporation (Netherlands).

VIS Spectra

Electronic spectra were recorded on a Perkin-Elmer Lamda 9 on ITO. Due to different reflections and scattered light, a background represented by a base line, assuming the absorptivity at 860 and 500 nm to be zero, was subtracted.

Charge/Discharge Measurements of Phthalocyanine Thin Film Electrodes

Thin films of *2* in polymers *4*, *5*, and *6* on gold disks were obtained by casting as described [35]. Films on ITO (ITO obtained from Matsuzaki Shinku Co. Ltd. with an electrical conductivity of ~20 S/square) were prepared analogously by casting from solutions in *N,N*-dimethylacetamide (DMA). The compositions of films of *2* in the polymers were 1 : 1 by weight; the thickness (~250 nm) was determined by the individual densities and coverages, and it was monitored with a Sloan Dektak II. Cyclic voltammetric measurements of the thin film electrodes in contact with 1 *M* HCl or 0.5 *M* H_2SO_4 were conducted as described [33, 35]. Thin films of polymeric phthalocyanines *3* were prepared by the reaction of 1,2,4,5-tetracyanobenzene with a graphite electrode covered by a thin copper film [33].

Measurements for Light-Induced Dioxygen Reduction at Thin Film Electrodes

For electrode preparation, ITO was cut into plates of 1 × 1.5 cm^2 and cleaned with distilled water and methanol. Solutions of 0.5×10^{-4} to 1.7×10^{-4} mol/L porphyrine *1* or *2* and 0.02 to 0.10 g/L of one of the polymers mentioned above in DMA or pyridine served as coating solutions. For electrode preparation, 10 to 70 μL was dropped on an ITO plate. The solvent was removed *in vacuo* at 70°C by using a glass tube oven. The film thickness was determined by the individual densities and coverage of the coated amounts, and it was monitored with a Sloan Dektak II A. Vapor deposited films were obtained by using a Veeco VE-770 vacuum system at 10^{-5} torr. After the appropriate coating procedure, one-third of the layer was taken off with DMA, leaving a 1 cm^2 electroactive area. A glass-covered copper wire was attached by using conducting adhesive Rex bond T-700 (Muramachi Kagaku Kogyo Kaisha, Japan). This connection and the nonactive electrode area was sealed with Ciba-Geigy Araldite Rapid epoxy resin. The photoelectrochemical experiments were performed in a gas-tight 10 mL glass cell by using a three-electrode cell with the appropriate working electrode, a saturated calomel electrode (SCE), a platinum counterelectrode, and conventional electrochemical equipment. The light source was a Ushio 500 W xenon arc lamp. Toshiba neutral density filters were used to vary the light intensity without changing the spectral distribution. The light intensity was measured with a Kipp & Zonen CA1-754373 instrument. The electrolyte was 0.5 *M* aqueous KNO_3 (pH 5). The corresponding oxygen concentration in the electrolyte was calculated from literature data [47] by assuming the validity of Henry's law. The gas mixture was bubbled through the cell for 20 min prior to each measurement. Current densities were calculated from the geometrical surface area of the electrode; all potentials are given versus NHE.

Measurements of Electrocatalytical Dioxygen Reduction

The synthesis of *1* and *3* (M = Fe) were performed on a RB-carbon support by the reaction of $FeCl_2$-loaded carbon with 1,2-dicyanobenzene or 1,2,4,5-tetracyanobenzene as described [48]. For the preparation of the $FeCl_2$-loaded carbon, 0.95 g RB-carbon and 0.08 g $FeCl_2 \cdot 4H_2O$ were ultrasonically treated while stirring for 15 min in 50 mL acetone. The solvent was evaporated and the product dried *in vacuo*. 85% of the $FeCl_2$ was adsorbed (Fe content of the carbon, 0.19%). The Fe-loaded carrier was reacted with dicyanobenzene (molar ratio 1 : 4) or tetracyanobenzene (molar ratio 1 : 2) at 300°C. The determination of the amount of *1* on carbon was carried out by dissolving *1* in concentrated H_2SO_4 and following quantitative electron spectroscopy. For the yield of the insoluble polymer *3*, the same yield as for *1* was assumed. The yield of *1* on carbon is 39% (loading of 10.6%). Samples were pyrolyzed for 2 h at 800°C under argon. The electrocatalytic measurements using finely dispersed catalysts were conducted with conventional equipment. As a working electrode, Au/Pt mesh (85/15) with a surface of 4 cm^2 was used. The reference electrode was SCE and the counter electrode was a Pt disk (1 cm^2). 100 mg of the catalyst was dispersed in 100 mL of 1 *M* aqueous KOH under stirring and ultrasonic treatment. The dispersion was added to 800 mL of 1 *M* KOH. Before starting the measurement, dioxygen was bubbled into the dispersion for 30 min. Current potential plots were recorded while stirring at 500 rpm. KOH solution without any catalyst was taken as the standard, and all listed values were normalized to this standard.

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