

Photoelectrochemical Behavior of a Hydroxyaluminum Phthalocyanine Polyvinylpyridine–Iodine Electrode

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Synopsis

A complex of poly-4-vinylpyridine with iodine is formed when a thin film of the polymer is immersed in a I_3^-/I^- redox couple solution. A hydroxyaluminum phthalocyanine photoelectrochemical cell presents short-circuit current up to $107.3 \mu A \text{ cm}^{-2}$ for a conversion efficiency of 0.035% when the organic film is coated with the polymer layer in an iodine/iodide electrolyte. This improvement is assigned to the contribution of the complex itself and to the decrease in the series resistance of the cell.

INTRODUCTION

The use of photovoltaic cells based on organic semiconductors is an interesting approach to solar energy conversion. Among these organic compounds, phthalocyanine materials have received special attention in photoelectrochemical cells.¹⁻¹⁶ Our laboratory is presently engaged in the broadening of the photoresponse and the enhancement of the electrical conductivity of a trivalent metal phthalocyanine: hydroxyaluminum phthalocyanine (PcAlOH).¹⁷⁻²⁰

Polymers have been used in conjunction with phthalocyanines for building thin film electrodes.²¹⁻²³ Polymers were used as binders in most of the cases, retaining mechanically the pigment particles in the form of a thin film. The effects of the polymers on the improvement of the cell performance have also been reported.²³ We report here the effect of polyvinylpyridine (PVPy) on the performance of a phthalocyanine photoelectrochemical cell. Polyvinylpyridine polymer was chosen for the following reasons: (a) effect of polyvinylpyridine on the phthalocyanine photovoltaic cell performance has been reported,²³ (b) complexes of polyvinylpyridine and iodine with low resistivities have been described,²⁴ and (c) photovoltaic properties of a poly-2-vinylpyridine- I_2 complex already have been studied.²⁵

EXPERIMENTAL

The hydroxyaluminum phthalocyanine (PcAlOH) was synthesized as described previously.^{18,19} The films are prepared by sublimation in a bell jar evaporator, the tin oxide (NESA) substrates (PPG Industries, sheet resistivity $\rho_s = 250 \Omega/\text{square}$) being placed 5 cm from the tantalum-boron nitride boat.

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The polymer deposition consists of dipping the electrode in a solution of poly-4-vinylpyridine (Polyscience, 1 wt % in methanol). The film is then allowed to dry in air.

The NESAs electrodes (2.5 cm \times 5.0 cm) were cleaned before sublimation coating by placing them in a detergent solution, followed by subsequent rinsing with tap water, distilled water, and methanol. An insulating polymer was used to define a 1.5 cm² active area. The contact with the substrate electrode was made with a copper wire and silver conducting paint (GC Electronics).

All chemicals used in this work were classified as high purity and used without further purification. They were dissolved in distilled water from a Corning Megapure water distillation system. All electrolytic solutions contained 0.1 M Na₂SO₄ and the pH was adjusted with hydrochloric acid. The electrolyte conditions were [BQ] = 2[HQ] = 4 \times 10⁻³ M at pH 2.5 for benzoquinone (BQ)/hydroquinone (HQ) redox couple and [I₃⁻] = 10⁻³, [I⁻] = 10⁻⁴ M at pH 1.5 for I₃⁻/I⁻ redox couple.

Absorption spectra were recorded with a LKB 4050 spectrophotometer interfaced to an Apple IIe computer.

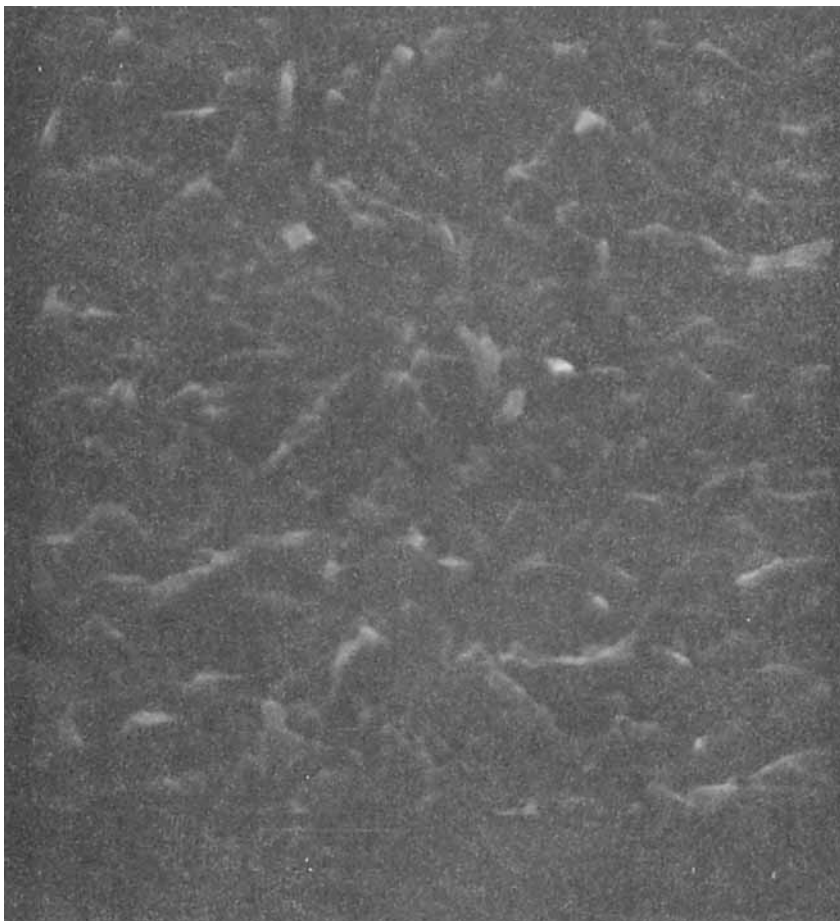
A conventional three-electrode single-compartment cell was used for the electrochemical measurements. A saturated calomel electrode (SCE) served as the reference and a Pt foil (8 cm²) as the counterelectrode. Electrolytic solutions were not deaerated and measurements were performed under ambient atmosphere. The working electrode was placed at about 2 mm from the cell window to minimize the light absorption by the solution. The organic film was always directly illuminated. The white light illumination source is the 300 W ELH tungsten-halogen lamp of a Kodak Ektagraphic slide projector (model AF2) giving an irradiation of 10 mW cm⁻². Monochromatic illumination was performed using a ISA H-20 monochromator. All action spectra were computed for the same photon flux incident on the film at each wavelength ($N_{\text{max}} = 2.7 \times 10^{14}$ photons cm⁻² s⁻¹) taking into account the measured light exponent, γ , at these energies.^{18,19}

The light intensity was measured using a United Detector Technology 21A powermeter equipped with a radiometric filter. All electrical measurements were performed in a Faraday cage. When used in the photogalvanic mode, the measurements were taken with a Keithley 616 electrometer; when used in the electrochemical and photoelectrochemical modes, the measurements were performed with a Model 362 potentiostat from Princeton Applied Research.

RESULTS

Surface Morphology

The surface morphology of sublimed films of PcAlOH has been already characterized elsewhere by scanning electron microscopy.¹⁸ SEM micrographs for a 300 Å thick PcAlOH film and for the same film coated with a poly-4-vinylpyridine layer are represented in Figures 1(a) and 1(b), respectively. The PcAlOH film is constituted of "noodles" of 1 μm in length and 0.1 μm in diameter. This morphology is independent of the thickness, and large empty areas are present between the "noodles." When coated with a poly-



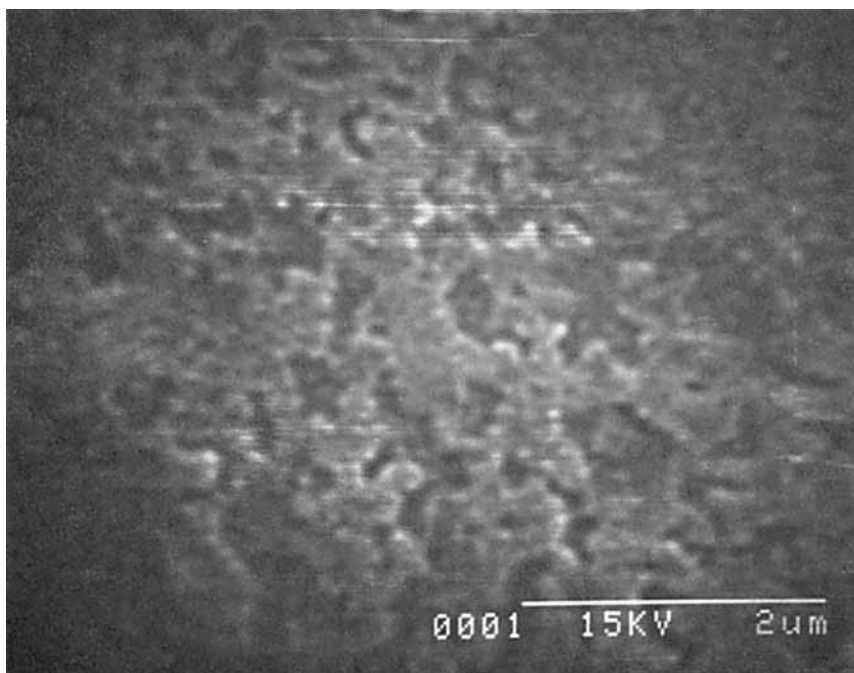
(a)

Fig. 1. Scanning electron micrograph of a PcAlOH film before (a) and after (b) coating with PVPy.

4-vinylpyridine layer, the film morphology changes radically, showing that the whole phthalocyanine surface is covered by the polymer film.

Absorption and Action Spectra

Thin, sublimed, hydroxyaluminum phthalocyanine films present a single broad absorption band at $\lambda = 640$ nm with a shoulder at $\lambda = 730$ nm, as shown in Figure 2(A) for a 300 Å thick PcAlOH film (curve a). The PcAlOH sublimed films are mainly of the α -form.¹⁷ When coated with the poly-4-vinylpyridine layer, the absorbance increases slightly (curve b). After one hour in the electrolyte solution containing the I_3^-/I^- redox couple, the absorption spectrum of the same electrode shows a large absorption region between 400 nm and 550 nm (curve c). This absorption is due to the interaction of the polymer with the redox couple; this interaction can be seen in



(b)

Fig. 1. (Continued from the previous page.)

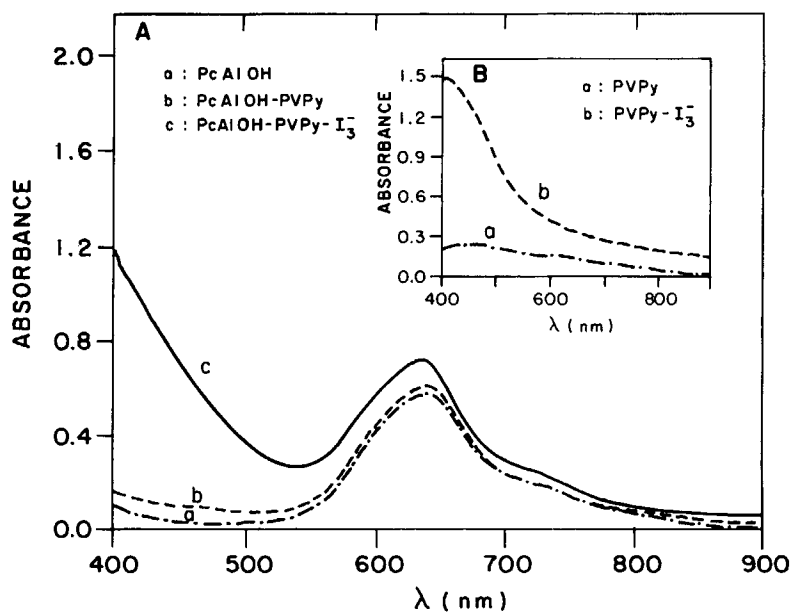


Fig. 2. Absorption spectra of thin films of PcAlOH (300 Å) and PVPy: (A) PcAlOH (a, ---), PcAlOH-PVPy before (b, ---), and after (c, —) contact with iodine. (B) PVPy before (a) and after (b) contact with iodine.

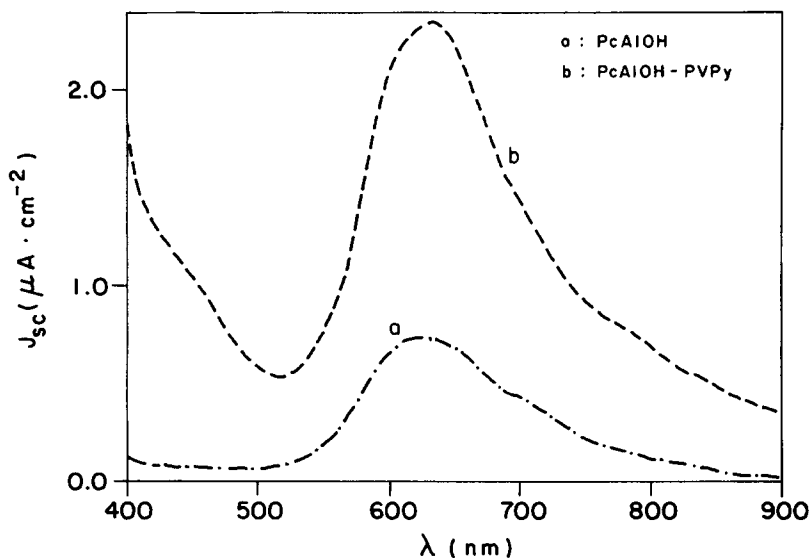


Fig. 3. Action spectra of NESAs/PcAlOH (a, ---) and NESAs/PcAlOH/PVPy (b, - · -) electrodes with I_3^-/I^- redox couple.

Figure 2(B) where curves are for a PVPy film deposited on a NESAs glass before (a) and after 1 hour (b) in the electrolyte. Curve 2b probably denotes the presence of a PVPy- I_2 complex absorbing at 408 nm.^{24,25} The final PcAlOH-PVPy- I_2 electrode shows an absorption spectra composed of two large bands of absorption, the 400–550 nm region being assigned to the PVPy- I_2 complex, while the 550–750 nm region is attributable to the PcAlOH itself.

Figure 3 depicts the action spectra for the NESAs//PcAlOH// I_3^-/I^- //Pt (curve a) and the NESAs//PcAlOH-PVPy// I_3^-/I^- //Pt (curve b) cells (the symbol // represents a phase boundary). The measured photocurrents must be corrected for the wavelength dependence of both the lamp intensity and the photodetector responses and for the variation of the short-circuit current (J_{sc}) with the light intensity I . This latter variation obeys the following equation²⁶:

$$J_{sc} = kI^\gamma \quad (1)$$

where k is a proportionality factor and γ is the light exponent of the cell. The values of γ are 0.95 for the cell without polymer and 0.92 for the same cell with the polymer layer, measured at $\lambda = 630$ nm. The corrected action spectrum is then describing the wavelength dependence of the short-circuit photocurrent for a constant photon flux at each wavelength, where:

$$J_{\lambda_{corrected}} = J_{\lambda_{measured}} \left(\frac{N_{max}}{N_\lambda} \right)^\gamma \quad (2)$$

N_{max} and N_λ being the maximum incident photon flux and the incident photon flux for the considered wavelength, respectively. The maximum pho-

ton flux is there $N_{\max} = 2.7 \times 10^{14}$ photons $\text{cm}^{-2} \text{ s}^{-1}$ for an irradiation directly incident on the solid-liquid interface.

The appearance of the action spectrum is very similar to that of the corresponding absorption spectra. However, the photocurrent peak delivered by the PcAlOH-PVPy electrode presents a clear increase compared to the PcAlOH electrode, as seen in Figure 3. The quantum efficiencies can be calculated from the action spectrum using the equation¹⁸:

$$\phi(\%) = 100J_{sc}(qN)^{-1} \quad (3)$$

where q is the electron charge and N the incident photon flux (here equal to N_{\max}). The quantum efficiency is the ratio of the number of collected electrons to the number of incident photons. The peak values are $\phi = 1.7\%$ for the PcAlOH electrode and $\phi = 5.5\%$ for the PcAlOH-PVPy electrode, giving an increase more than 300%. This improvement in the photocurrent delivered by the PcAlOH-PVPy electrode might be attributed to a better electron transfer from the electrode to the redox couple.

Current-Voltage Characteristics

Despite the interesting photovoltaic characteristics of the poly-2-vinylpyridine,²⁵ the poly-4-vinylpyridine (PVPy) delivers only poor currents and voltages when deposited on NESAs and immersed in an electrolyte containing redox couples. Table I reports the short-circuit current and the open-circuit voltage for NESAs/PVPy/redox/Pt cell under white light irradiation, for the benzoquinone/hydroquinone and iodine/iodide redox couples.

Figure 4 shows the current voltage (J - V) characteristics of the photoelectrochemical cells; curves a and b are for a NESAs/PcAlOH/ I_3^-/I^- /Pt cell in the dark (a) and under white light illumination (b), and curves c and d are for a NESAs/PcAlOH-PVPy/ I_3^-/I^- /Pt cell in the dark (c) and under the same illumination (d) ($I = 10 \text{ mW cm}^{-2}$). The J - V curves in the dark present good rectifications, the rectification ratios, at 0.12 volt, being 25 for the PcAlOH film and 49 for the PcAlOH-PVPy film. When the electrodes are irradiated under white light, cathodic photocurrents appear, showing that the electrons coming from the organic film are reducing the iodine in solution.

When the PcAlOH film is covered with the PVPy layer, we can note three interesting differences in the J - V curves: (1) the current under illumination increases in the whole potential range; (2) the slope of the curve in the forward region increases; and (3) the dark current of the PcAlOH-PVPy shows large values for potential more than 0.2 volt in the reverse region.

The intersection of the J - V curves under illumination with the currents and voltages curves gives the short-circuit current J_{sc} and the open-circuit

TABLE I
Electrical Characteristics of a PVPy Electrode

Redox couple	J_{sc} ($\mu\text{A cm}^{-2}$)	V_{oc} (mV)
BQ/HQ	-0.005	0
I_3^-/I^-	0.1	48

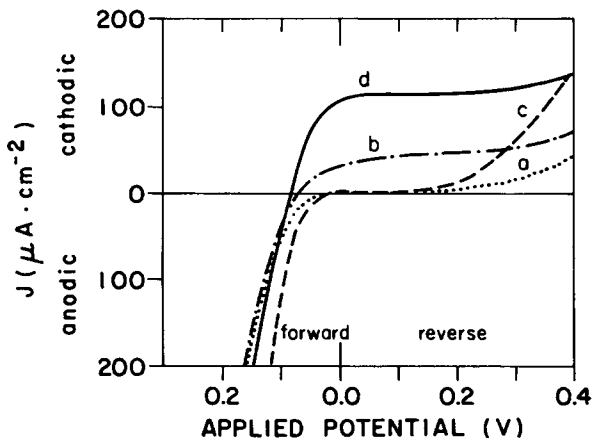


Fig. 4. Current-voltage characteristics of a PcAlOH electrode in the dark (a, ...) and under white-light illumination (b, ---), and of the same electrode coated with PVPy, in the dark (c, ---) and under illumination (d, —). Redox couple I_3^-/I^- , $I = mW \cdot cm^{-2}$.

voltage V_{oc} , respectively. The fill factor can be calculated as follows:

$$ff = \frac{(J-V)_{max}}{J_{sc} \cdot V_{oc}} \tag{4}$$

The conversion efficiency is then given by:

$$\eta(\%) = 100 J_{sc} V_{oc} ff(I)^{-1} \tag{5}$$

The value of J_{sc} , V_{oc} , ff , and η are presented in Table II for the two electrodes.

The slopes of the $J-V$ curves under forward polarization in the dark are quite different: these curves follow the equation¹⁸:

$$J = J_0 \left[\exp \frac{q(V - R_s I)}{nkT} - 1 \right] + \frac{V - R_s I}{R_{sh}} \tag{6}$$

where J_0 is the exchange current density, n is a variable parameter, q is the electron charge, and R_s is the series resistance of the electrochemical cell. This expression is very similar to the equation describing the dark $J-V$ characteristics of a Schottky barrier at a metal-semiconductor junction.²⁷

For $V \geq 3kT/q$, the last term in brackets can be neglected. If $R_s = 0$, a plot of $\ln J$ versus V yields a straight line with J_0 as intercept. n is deduced from

TABLE II
Electrical Characteristics of PcAlOH and PcAlOH/PVPy Electrodes with I_3^-/I^- Redox Couple

Electrode	J_{sc} ($\mu A \cdot cm^{-2}$)	V_{oc} (mV)	ff	η (%)	J_0 ($\mu A \cdot cm^{-2}$)	n	R_s (Ω)
PcAlOH	32.0	69	0.35	0.008	0.66	0.85	120
PcAlOH/PVPy	107.3	85	0.38	0.035	4.45	1.23	40

TABLE III
Effect of the Redox Couple on the Electrical Characteristics of a PcAlOH/PVPy Electrode

Test no.	Redox Couple	J_{sc} ($\mu\text{A cm}^{-2}$)	V_{oc} (mV)	ff	η (%)
1	BQ/HQ	34.0	90	0.38	0.011
2	I_3^-/I^-	90.0	89	0.42	0.034
3	BQ/HQ	50.7	115	0.39	0.023

the slope. If $R_s \neq 0$, its value can be calculated from the off-linearity deviation at high voltage bias. We report in Table II the values of J_0 , n , and R_s for the two types of films. One can notice mainly that the series resistance is three times lower for a PVPy-coated phthalocyanine film compared with a bare PcAlOH film.

The effect of the interaction of PVPy with iodine can also be seen in Table III, where the short-circuit currents, the open-circuit voltages, the fill factors, and the conversion efficiencies are reported for a NESA//PcAlOH-PVPy//redox//Pt cell. The photoelectrochemical cell was first characterized in the electrolyte containing BQ/HQ as redox couple (Table III, Test No. 1), then in the I_3^-/I^- redox couple solution (Table III, Test No. 2). An increase of the short-circuit current is noticed, leading to a better light-to-electricity conversion. The two redox couples in the electrolyte conditions present the same value for the redox potential, $E_{\text{red}} = 0.29$ V/SCE. α -PcAlOH electrodes usually deliver similar currents and voltages in either redox couple.¹⁹ Since the absorption band of the complex appears and stabilizes in less than one hour, the improvement in the short-circuit current must be due to the presence of the PVPy- I_2 complex on the electrode. The same electrode in BQ/HQ solution presents higher values of current and voltage after its contact with the I_3^-/I^- solution (Table III, Test No. 3).

DISCUSSION

The absorption spectra of the PVPy films deposited on NESA glass or PcAlOH thin film seem to demonstrate the formation of a PVPy- I_2 complex when in contact with the iodine/iodide redox couple. A broad absorption band with a peak at 389 nm has been observed with poly(4-vinylpyridine)-iodine complex film prepared on a quartz slide.²⁴ A similar band at 400 nm was noticed by Vander Donckt et al. for their poly(2-vinylpyridine)-iodine complex.²⁵ In these two cases, the complexes were formed by interaction of the solid polymer with iodine vapor or with a solvent containing iodine. In this work, the PVPy- I_2 complex is formed by interaction of the polymer film with the electrolyte containing the iodine/iodide redox couple ($\text{I}_3^- = 10^{-4}\text{M}$).

The highest $[\text{I}_2]/[\text{polymer}]$ ratio (1.8–2.0) in the complex gave the highest current ($J_{sc} = 99.6 \mu\text{A cm}^{-2}$)²⁵ and the lowest resistivity.²⁴ A NESA//PVPy- I_2 //Pt photovoltaic cell yielded a conversion efficiency of 0.05% for a white light intensity of 2 mW cm^{-2} .²⁵ The transformation yield of white light (10 mW cm^{-2}) into electricity for our NESA//PcAlOH-PVPy// I_3^-/I^- //Pt cell is 0.035%, one of the highest values for organic photoelectrochemical cells.

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