

Electrochimica Acta 45 (2000) 2227-2239

electrochimica

www.elsevier.nl/locate/electacta

The electrochemistry of platinum phthalocyanine microcrystals I. Electrochemical behaviour in acetonitrile electrolytes

Junhua Jiang, Anthony Kucernak *

Department of Chemistry, Imperial College, London SW7 2AZ, UK

Received 27 August 1999; received in revised form 13 December 1999

Abstract

Platinum phthalocyanine (PtPc) microcrystals deposited upon platinum, glassy carbon and gold by a process of dry abrasion have been characterised by electrochemical techniques. This mechanical abrasion can produce good electronic contact and adhesion between the microcrystals and the electrode. The redox process of PtPc microcrystals is accompanied by two reversible electrochemical phase transformations, evidenced by a sharp peak and unusually large peak potential differences. Similar to conductive polymers, an obvious first-scan discrepancy and large capacitance are observed during electrochemical oxidation. Some of the intercalated anions remain in the re-reduced microcrystals and lead to a conductivity enhancement of the microcrystals, supported by AC impedance and X-ray photoelectron spectroscopy (XPS) results. Coulometry shows that the size of the anion determines the rate and degree of oxidation, and influences the reversible phase transformations. Chronoamperometry shows diffusion-controlled nucleation and growth kinetics, controlled by the diffusion of anions into the solid films. The conformational relaxation model was used to describe this process. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Platinum phthalocyanine; Electrochemical behaviour; Phase tranformation; Microcrystals; Abrasion

1. Introduction

The electrochemical and photochemical properties of metallophthalocyanine (MPc) have been extensively studied because of their characteristic molecular structure. Both applied and fundamental studies have been reported [1,2], and these materials have been applied successfully to electrochromic devices [3,4], organic solar cells [5], switching devices [6] and power sources [7–9]. An extensive review of phthalocyanine electrochemistry has been presented [10].

Compared with the first-row transition metal phthalocyanines, precious metal phthalocyanines have higher thermal stability and more effectively resist electrochemical and chemical oxidation [11]. Platinum phthalocyanine (PtPc) has been investigated as a charge transfer salt [12–14] and electro-catalyst for oxygen reduction [11,15–17]. Electrochemically doped PtPc shows highly metal-like conductivity [12]. Deposition of PtPc onto an inert substrate has been achieved through both its evaporation in vacuum and through encapsulating PtPc microcrystals in a polymer matrix [11–13], although it is difficult to obtain good electrode reproducibility using the above two methods. The electrochemical characterisation of PtPc has been limited

^{*} Corresponding author.

^{0013-4686/00/\$ -} see front matter 0 2000 Elsevier Science Ltd. All rights reserved. PII: S0013-4686(00)00318-2

because of its low solubility even in organic solvent at high temperature. PtPc dissolved in 1-chloronaphthalene at 150°C produces two reduction waves at -1.23 and -1.61 V against a Fe(C₅H₅)₂ reference electrode [18]. A new composite electrode PtPc-polybisphenol-A-carbonate reticulate structure is characterised by two anodic and four cathodic redox transitions in propylene carbonate electrolyte [12].

In this work, a systematic study of the electrochemical behaviour in acetonitrile of PtPc microcrystals attached by a process of dry abrasion to an electrode surface without the need of a polymeric binder is described. A recent review of voltammetry of solid microparticles immobilized on electrode surfaces provides useful background to the techniques for immobilizing powders on electrodes [19].



Fig. 1. SEM images of a thin composite platinum phthalocyanine (PtPc)-polybenzimidazole (PBI) film (a) and of an abrasively obvious PtPc layer on a glassy carbon electrode (b). In the latter, loosely adherent PtPc particles (white) rest on a dense PtPc layer covering the entire glassy carbon electrode.

2. Experimental

2.1. Chemicals and instrumental

Tetrabutylammonium perchlorate $(TBAClO_4,$ Fluka), tetrabutylammonium tetrafluoroborate (TBA-BF₄, Aldrich) and tetrabutylammonium hexafluorophosphate (TBAPF₆, Fluka) were of electrochemical grade and used as received. Acetonitrile (AN, Analar) was distilled under vacuum into a flask filled with the molecular sieve. PtPc was synthesized by heating finely crushed phthalonitrile and PtCl₂ at 200°C in the absence of a solvent for one hour [10]. Two separate sublimation steps purified the product, each repeated three times. In the first, unreacted phthalonitrile was sublimed from the crude product at 140°C and 0.1 mbar pressure, and in the latter, PtPc was sublimed from the crude product at 550°C and 0.1 mbar pressure.

Voltammetric, chronoamperometric and coulometric measurements were performed at room temperature (~20°C) using an Autolab General Purpose Electrochemical Systems (GPES, Ecochemie, Netherlands). The electronic conductivity of the PtPc powder microcrystals was measured using an Autolab Frequency Response Analyser (FRA). A following paper will describe AC impedance experiments. X-ray photoelectron spectroscopy (XPS) was measured using a Kratos XSAM 800 ultrahigh vacuum photoelectron spectrometer using the Mg K α line as the excitation source.

Electrochemical measurements were performed in an oxygen-free three-compartment electrochemical cell. The reference half-cell was $Ag/10^{-3}$ mol dm⁻³ AgNO₃ + 0.1 mol dm⁻³ TBACIO₄ + AN, and the counter electrode was a platinum foil. Solutions were deoxygenated with high purity argon.

2.2. The preparation of PtPc microcrystals electrode

A gold disk (0.5 mm diameter, 99.99%, Goodfellows, UK), platinum disk (0.5 mm diameter, 99.95%, Goodfellows, UK) or glassy carbon (5 mm diameter, Sigadur G, Hochtemperatur Werkstoffe GmBH, Germany) served as the working electrode.

SEM images (Fig. 1(a)) of PtPc fixed onto a glassy carbon substrate using polybenzimidazole (PBI) showed needle-like microcrystals with an average diameter of $10-20 \ \mu m$.

Microcrystals of PtPc were attached to the electrode surfaces without polymer binder as follows. First, a small amount of the microcrystal powder was placed on a smooth glass plate. The electrode was then rubbed heavily on the powder covered glass until the electrode surface was thoroughly coated by a thin-layer of PtPc. Successful coating was evidenced by a shiny purple colour. Finally, the electrode was transferred to the electrochemical cell containing non-aqueous electrolyte.



Fig. 2. Cyclic voltammograms of platinum phthalocyanine (PtPc) microcrystals on a glassy carbon electrode in 0.1 mol dm⁻³ tetrabutylammonium perchlorate (TBAClO₄) + acetoni-trile (AN) ($\nu = 50 \text{ mV s}^{-1}$). —, the first scan; ----, the second:---, the fifth.

The microcrystals were found to have good electronic contact and adhesion with the substrate, and electrodes produced in this manner show good reproducibility. The amount of PtPc film on the electrode surface was measured by coulometry after exhaustive electrolysis. The coulometric measurements were calibrated by dissolving the deposited microcrystals in 1-chloronaph-thalene and measuring the absorbance at λ_{max} (650 nm) on the basis of the measured extinction coefficient (lg $\varepsilon = 5.18$), finding a good linear relationship between the two. This extinction coefficient is consistent with those reported for other MPcs in the same medium [20]. The thickness of PtPc film was calculated to be in the range of 5–10 µm on the basis of a PtPc density of 1.96



Fig. 3. Cyclic voltammograms with different potential ranges for platinum phthalocyanine (PtPc) microcrystals on a glassy carbon electrode in 0.1 mol dm⁻³ tetrabutylammonium perchlorate (TBACIO₄) + acetonitrile (AN) ($\nu = 50$ mV s⁻¹).

g cm⁻³ [21,22]. An SEM image of the mechanically deposited PtPc microcrystals on a glassy carbon substrate is shown in Fig. 1(b). The mechanically deposited PtPc is found to uniformly coat the entire surface, with small excess particles loosely adherent to the top layer. SEM images of cross-sections through the film do not show excessive porosity. The mechanical abrasion has severely broken the microcrystals and damaged their external faces. There was no evidence of recrystallisation of the material after potentiodynamic cycling. Electrodes prepared in this way exhibit the purple metallic sheen indicative of PtPc. All of the results presented in the following paper will be from electrodes prepared in this manner.

Application of Nafion to selected electrode surfaces was readily achieved by dropping 5 μ l 5% (wt.%) Nafion[®] solution (Aldrich) onto the PtPc covered glassy carbon surface. The recast film was dried at room temperature.

After each series of experiments, the electrode surfaces were renewed by polishing and cleaning with acetone and Millipore water. The cleaned electrodes were dried in an oven at 80°C.

3. Results

3.1. General electrochemical behaviour

Cyclic voltammograms of PtPc microcrystals on glassy carbon in 0.1 mol dm⁻³ TBAClO₄ + AN are shown in Fig. 2. There is a large difference between the first and successive scans, which we will comment upon below. The following discussion considers the voltammetry of the film after the first scan.

On increasing the potential the oxidation current rises at about 0.20V and grows gradually with potential until about 0.60 V. There is a broad difficult to measure peak (1) occurring in the range (0.2-0.6 V). The current then grows rapidly and reaches a maximum (peak 2) at about 0.75 V. At higher potentials, peak 3 is seen at 1.07 V accompanied by peak 3' at about 1.14 V. There is a long flat-current region between peak 2 and peak 3. On reversing the scan four peaks are seen. A very small peak (4) at 0.82 V is followed by a sharp peak (5) at 0.67 V; a rather broad peak (6) at about 0.40 V is followed by a small peak (7) at 0.06 V.

Fig. 3 displays the cyclic voltammograms with different upper potential limits for PtPc micro-crystals on the glassy carbon electrode in 0.1 mol dm⁻³ TBAClO₄ + AN. Peaks 1 and 6 correspond to a chemically reversible couple. The potential difference between the two peaks is estimated to be 0.15 V. Peak 2 is responsible for peak 7. The potential difference between these two peaks is unusually large at 0.71 V. Peak 2 shows a larger peak current and peak area than peak 7, and so



Fig. 4. Cyclic voltammograms at 5 mV s⁻¹ for platinum phthalocyanine (PtPc) microcrystals deposited on to a glassy carbon electrode in 0.1 mol dm⁻³ tetrabutylammonium perchlorate (TBAClO₄) + acetonitrile (AN).

it must be expected that some of the charge associated with peak 2 is also recovered in peak 6. Peak 3 leads to the formation of peak 5 with a small shoulder at peak 4. The potential difference between peak 3 and peak 5 is about 0.42 V. Furthermore, an unusually large double-layer current is observed in the flat-current region between peak 2 and peak 3, compared to the double layer current at the re-reduced electrode (E < 0 V). Lastly, besides an obvious influence on the height and potential of peak 4 and peak 5 the oxidation potentials around peak 3 have an influence on the peak potential of peak 7. A more positive potential leads to a shift of peak 7 to more negative potentials.

The ratios of the anodic to cathodic charge are independent of the upper potential limit and remain close to 1. This ratio implies that every electrochemical step is chemically reversible.

A cyclic voltammogram at low scan rates for PtPc micro-crystals on the glassy carbon electrode in 0.1 mol dm⁻³ TBAClO₄ + AN is shown in Fig. 4. It is found that the scan rate has an influence on the peak shape. Peak 2 and peak 3 have a smaller half-height width at lower scan rates than at high scan rates. The peak current is proportional to the scan rate to the power of

Table 1

The anodic charge (Q_a) , cathodic charge (Q_c) and their ratios (Q_c/Q_a) for successive five scans

Scan no.	$10^3 Q_{\rm a}/C$	$10^3 Q_{ m c}/C$	$Q_{ m c}/Q_{ m a}$
1	2.85	2.35	0.82
2	2.50	2.42	0.97
3	2.43	2.40	0.99
4	2.42	2.40	0.99
5	2.42	2.41	1.0

~ 0.7–0.8 for scan rates in the range of 5–100 mV s⁻¹, rather than being proportional to the scan rate or its square root. The charge involved both in oxidation and reduction is independent of the scan rate.

3.2. First scan discrepancy in the voltammetry

The voltammetry of the PtPc microcrystals changes considerably after the first scan. Compared to following scans, little oxidation occurs at peak 1 in the potential range 0.2–0.6 V during the first scan. However, peak 6, which is the corresponding reduction process, does not alter in magnitude between the first and successive scans, suggesting that the process responsible for peak 1 still occurs, although presumably at higher potentials. In support of this, peak 2 shows a larger magnitude while also occurring at a higher potential (0.8 V) than successive scans. Furthermore, the flat-current region between peaks 2 and 3 is not evident during the first scan. Peak 3 occurs at the same potential but is slightly decreased in size whereas peak 3' is significantly decreased in size and slightly shifted in potential. The peaks due to reduction of the film are essentially the same as seen after further scans, except peak 5, which shows a smaller current during the first scan.

The anodic charge (Q_a) , cathodic charge (Q_c) and their ratios (Q_c/Q_a) for five successive scans over the full potential range are listed in Table 1. The anodic charge is larger than the cathodic charge during the first scan with an anodic charge excess of 0.35 mC. There are two possibilities for this difference. One is that the original electrochemical reaction is not chemically reversible. The other is that there is some physical loss of material during the oxidation. The anodic charge is almost equivalent to the corresponding cathodic charge during subsequent successive scans, and charge reversibility is maintained.

In order to rule out the possibility of physical loss of PtPc microcrystals during scanning, a thin Nafion film was applied to cover the PtPc coating on the electrode. A similar first-scan effect can still be seen from the cyclic voltammograms of Nafion coated PtPc microcrystals on glassy carbon in 0.1 mol dm⁻³ TBAClO₄ + AN, shown in Fig. 5. The recast Nafion film is sparsely cross-linked and has poor ion-selectivity because of a large number of pinholes [23], and as a result the anions can easily penetrate the film. The first-scan effect is also observed on a PBI-PtPc composite film electrode [24]. These similar first-scan effects indicate that the anodic charge loss was caused by chemical irreversibility of the first scan rather than by the physical loss of PtPc micro-crystals from the electrode surface.

The significant difference between the first and successive scans has also been reported in the voltammograms of polyaniline [25,26]. Aoki et al. explained this effect on the basis of a percolation threshold poten-



Fig. 5. Cyclic voltammograms for Nafio-coated platinum phthalocyanine (PtPc) microcrystals deposited on to a glassy carbon electrode in 0.1 mol dm⁻³ tetrabutylammonium perchlorate (TBACIO₄) + acetonitrile (AN) ($\nu = 50$ mV s⁻¹). —, first scan; -··-, second scan.

tial [27]. Fig. 6 shows the dependence of the conductivity of PtPc microcrystals on potential measured using a.c. impedance. The original PtPc is a semi-conductor and has low conductivity. The conductivity only slightly increases with potential up to 0.6 V. An abrupt growth in conductivity occurs at about 0.7 V, at the same point at which the oxidation current begins to grow rapidly during the first scan in Fig. 2. It is well accepted that it is difficult to initiate electrochemical reactions at materials with insulating or semiconducting films at which electron transfer through that film is hindered. In such situations the electron has to be transferred at the electrode/film interface, while at the same time counterions have to cross the electrolyte/film interface in order to maintain charge neutrality within the film. In order to incorporate anions into the PtPc films, conducting pathways through the polymer layer have to be nucleated [28]. Once there is sufficient overvoltage for this process, the oxidation can proceed



Fig. 6. Dependence of AC conductivity of deposited platinum phthalocyanine (PtPc) microcrystals on the applied potential.

rapidly giving sharp voltammetric peaks. The conductivity of PtPc microcrystals at the open circuit potential (-0.22 V) increases from $2.9 \times 10^{-3} \text{ S cm}^{-1}$ to $2.1 \times 10^{-2} \text{ S cm}^{-1}$ after one scan, as measured by electrochemical impedance in the following paper. This higher conductivity facilitates electrochemical oxidation at the electrochemically cycled PtPc microcrystals. The conductivity enhancement of normal semiconductors can be achieved through doping, and it is possible that the PtPc semiconductor studied here undergoes a doping process through an electrochemical cycle and that some anions remain in the cycled film to permanently dope the PtPc semiconductor.

The incomplete removal of anions from a MPc film after potential cycling has been previously reported [29]. The presence of anions in re-reduced PtPc films have been confirmed by XPS for systems in which perchlorate is the anion (the detection limits for phosphorus and boron are too low to allow comparison with the PF_6^- and BF_4^- anions). The re-reduced sample was taken out from the electrolyte and rinsed multiple times with fresh acetonitrile. Typical surface spectra for the original film and the re-reduced sample are shown in Fig. 7. The presence of chlorine (Cl_{2p} at 204 eV) is evident in the re-reduced film.

3.3. The effect of electrode substrate

To test if the electrode material has any effect on the voltammetry of PtPc microcrystals, three different electrodes were used as substrates (5 mm diameter glassy carbon, 0.5 mm platinum, 0.5 mm gold). In all cases, the responses were almost identical, with voltammetric



Fig. 7. X-ray photoelectron spectroscopy (XPS) spectra for untreated platinum phthalocyanine (PtPc) microcrystals (a), and for electrochemically oxidised and then reduced microcrystals (b).

Table 2

The peak	parameters	for	platinum	phthalocyanine	(PtPc)	microcrystals	on	different	electrode	substrates	in	0.1	mol
tetrabutyla	ummonium p	erch	lorate (TB	$AClO_4$) + acetoni	trile (A	N) at 50 mV	s^{-1}	after five	cycles				

Electrode	Peak po	Peak potentials (E_p/V)						Peak potential difference $(\Delta E_p/V)$		
	$\overline{E_{\mathrm{p},1}}$	$E_{\rm p,2}$	$E_{\rm p,3}$	$E_{\rm p,5}$	$E_{\rm p,6}$	$E_{\rm p,7}$	$\Delta E_{\mathrm{p1,6}}$	$\Delta E_{\mathrm{p2,7}}$	$\Delta E_{\mathrm{p3,5}}$	
Glassy carbon	0.535	0.751	1.084	0.663	0.385	0.040	0.150	0.711	0.421	
Platinum	0.514	0.688	1.035	0.652	0.395	0.038	0.119	0.650	0.383	
Gold	0.517	0.676	1.026	0.653	0.380	0.052	0.131	0.624	0.373	

steady states being achieved within five cycles. For ease of comparison, typical peak parameters are summarised in Table 2. The different peak currents are dependent upon the electrode area and the loading of PtPc microcrystals on the electrode. Within experimental error and the effect of uncompensated Ohmic drop, the peak parameters for redox reactions are independent of the underlying electrode materials. This strongly suggests that the phenomena we have reported above are associated with the bulk of the PtPc microcrystals rather than at the interface between the electrode and microcrystals.

3.4. The effect of charge compensating anion

To maintain the charge balance inside PtPc microcrystals, anions have to be incorporated during the oxidation process and must be expelled from the solid during the reduction process. The influence of anions on the redox behaviour of transition-metal phthalocyanine has been reported by some authors. Faulkner et al. reported that the size of anions affected their ability to enter the molecule, which determines the rate and degree of the oxidation of MgPc and ZnPc [29,30]. Toshima et al. found that the electrolyte anions play an important factor in the reversibility of electrochromism of CuPc [31]. In order to accomplish reversible electrochromism of CuPc film, the anion should be stable at the most positive voltage applied, and its Stokes radii should not be too large. Moreover, an anion that is too small is not suitable for reversible electrochromism, because a small anion easily remains within the film, even after reduction.

 PF_6^- , ClO_4^- and BF_4^- are spherical ions and are poorly solvated in acetonitrile [32,33]. Their size decreases from PF_6^- to BF_4^- ($r_i(PF_6^-) = 0.301$ nm, $r_i(ClO_4^-) = 0.290$ nm, $r_i(BF_4^-) = 0.284$ nm) [34]. Their Stokes Radii also decrease in this sequence [31]. The voltammetric responses with different potential ranges after 5 cycles were recorded for each of these different anions using the tetrabutyl ammonium cation. Fig. 8 shows cyclic voltammograms with different potential upper limits for PtPc microcrystals on the glassy carbon electrode in 0.1 mol dm⁻³ TBABF₄ + AN (a), and 0.1 mol dm⁻³ TBAPF₆ + AN (b), respectively. Compared with the curves in Fig. 3, the BF_4^- curves have similar characteristics except a smaller shoulder at peak 4, while the PF_6^- curves show more significant differences. The PF_6^- voltammogram shows an additional oxidation peak at about 1.18 V. This peak is responsible for two reductive peaks during the reverse scan. These peaks indicate that the doping and undoping of PF_6^- produces a more complicated phase transformation.

 dm^{-3}

Comparing the voltammetric response for the three different anions it was seen that the peak potentials are anion dependent. The potentials of peak 2 and peak 3 shift positive with the anion size. This indicates that it is difficult to drive large anions into the PtPc crystals. The potentials of peak 7 also shift positively with the anion size, indicating that it is relatively easy to expel large anions during the reduction of the film.

The effect of anions with different size on the extent of oxidation of the PtPc film was determined by using chronocoulometry. The number of electrons transferred per PtPc molecule obtained at different potentials as a function of anion are collected in Table 3. The oxidation extent increases as the anion size decreases at the same potential and increases with the oxidation potential. The BF_4^- anion is small enough to occupy more interlayer positions than the larger PF_6^- anion which is only able to occupy some larger sites within the crystal structure.

3.5. The anion concentration dependence

Bond et al. examined redox cycling of 7,7,8,8, tetracyanoquinodimethane (TCNQ) nanocrystals immobilized on a variety of electrodes in aqueous solutions [23]. They observed an 'inert zone' between the chemically reversible oxidation and reduction peaks of one of the redox couples of TCNQ. This significant separation between peaks is strikingly similar to the results that we have presented for PtPc microcrystals. By employing a random array of microelectrodes (RAM) electrode, they were able to examine the electrochemistry of the immobilized TCNQ crystals in solutions that varied by over four orders of magnitude in potassium chloride concentration without the effects of excessive Ohmic drop in solution. From these results they were able to measure a shift in potential of close to 60 mV decade⁻¹ for both the anodic and cathodic peaks.

Cyclic voltammograms with Ohmic drop correction for PtPc films on glassy carbon in $\text{TBACIO}_4 + \text{AN}$ solution with different CIO_4^- concentration are shown in Fig. 9. The oxidation charge increases with the electrolyte concentration, but the peak current is not proportional to the concentration. Because both peak 2 and peak 3 are caused by the nucleation and growth of a new phase within the PtPc film (see below), the concentration effect indicates that ClO_4^- is involved in the nucleation and growth kinetics occurring at these potentials. Peak 2 and peak 3 have a negative potential shift of about 27 mV decade⁻¹ and 18 mV decade⁻¹ of concentration, respectively. Some authors emphasized the role of junction potential and ionic activities in the comparative study of voltammetric response at various concentrations [35]. The potential of Ag/Ag⁺ is mainly determined by the concentration of Ag⁺ in the reference half-cell and is not affected by the concentration



Fig. 8. Cyclic voltammograms with different potential ranges for platinum phthalocyanine (PtPc) microcrystals on a glassy carbon in 0.1 mol dm⁻³ tetrabutylammonium tetrafluoroborate (TBABF₄) + acetonitrile (AN) (a) and in 0.1 mol dm⁻³ tetrabutylammonium hexafluorophosphate (TBAPF₆) + AN (b) ($\nu = 50$ mV s⁻¹).

Table 3 Electrons transferred per phthalocyanine molecule (*n*) for the oxidation of PtPc microcrystals at different potential in 0.1 mol dm⁻³ tetrabutylammonium salt of the respective anion + acetonitrile (AN)

Anions	<i>n</i> ₁ (0.6 V)	n ₂ (0.9 V)	n ₃ (1.2 V)
BF_4^-	0.25	0.43	0.68
ClO_4^-	0.17	0.27	0.45
PF_6^-	0.09	0.22	0.30

of anions. The influence of junction potential on the peak potential can be ruled out for the system. Similarly, the ionic activity coefficient of the electrolyte should have no great contribution to the change of the peak potential, as it varies by no more than a factor of three over this concentration range [36]. Therefore the above peak shifts imply that the ClO_4^- in the solution indirectly takes part in the phase transformation.

3.6. Chronoamperometric evidence for nucleation/growth kinetics

The chronoamperograms obtained when potential steps are applied to conducting polymers in different electrolytes and solvents have been modelled theoretically from several different points of view, including nonmetal-metal transitions in the amorphous phase [37], solid state electrochemical reactions [38], the introduction of a percolation threshold potential [24], and conformational relaxation control [39].

Evidence for nucleation/growth kinetics during the oxidation is provided by chronoamperometric (single potential step) experiments. The current-time transients at different potential steps are shown in Fig. 10. All experiments are stepped from the reduced state of the film at 0 V to a different oxidising potential. The curve at 0.65 V appears to be diffusion-controlled. In comparison, the step to 0.7 V shows significant differences at short time, while at longer time intervals the response is similar to the 0.65 V transient. The response can be considered as being due to the overlap of a peak at short time intervals and a curve similar to that occurring at 0.65 V. Because the electrochemical oxidation of the PtPc film is not adsorption-controlled, the overlapping peak provides evidence of the nucleation and growth of a second phase within the film. Increasing the step potential to 0.75 V results in a shortening of the duration of this phase transformation. When the potential reaches 1.0 V, the first transformation occurs so quickly that it is lost in the double layer charging transient, and the response again looks similar to that obtained at 0.65 V. Performing the experiment with a step potential of 1.1 V provides evidence of another nucleation and growth transient at short times when compared to the 1.0 V transient. Therefore, the doping of the PtPc film undergoes two independent solid-solid phase transformations occurring via nucleation/growth mechanisms. These electrochemical transformations are potential dependent and high overpotentials shorten the relaxation time. The current at longer time has a linear relation with $t^{-1/2}$. This indicates that the electrochemical processes are completed under diffusion control.



Fig. 9. Cyclic voltammograms for platinum phthalocyanine (PtPc) microcrystals deposited on a glassy carbon electrode tetrabutylammonium perchlorate (TBAClO₄) + acetonitrile (AN) as a function of electrolyte concentration ($\nu = 5 \text{ mV s}^{-1}$). —, 0.001 mol dm⁻³; ----, 0.01 mol dm⁻³; ----, 0.01 mol dm⁻³; ----, 0.01 mol dm⁻³.



Fig. 10. Current-time transients at different potentials for platinum phthalocyanine (PtPc) microcrystals deposited on a glassy carbon electrode in 0.1 mol dm⁻³ tetrabutylammonium perchlorate (TBAClO₄) + acetonitrile (AN).

Usually systems which undergo nucleation/growth kinetics display inductive loops in their voltammetry immediately after scan reversal [40]. One might expect to see such inductive loops in the scans in which the potential reverses part way up peaks 2 and 3 in Fig. 3. However, no such phenomenon is evident. Such an absence is possible when a large number of nucleation sites are formed and the growing sites collide at an early stage of growth. In such a case, the diffusion zones surrounding the growing zones quickly overlap, and there is no maxima on reversing the scan direction [40].

4. Discussion

For many MPc complexes, it seems likely that the oxidation and reduction take place reversibly on the phthalocyanine ring [41,42]. It would seem plausible that the electrochemical oxidation occurring on the PtPc involves reversible insertion of anions from the electrolyte to maintain overall charge neutrality, implying an overall reaction of the form

$$\operatorname{PtPc}_{(\text{solid})} + n\operatorname{ClO}_{(\text{solution})}^{-} \rightleftharpoons \operatorname{PtPc}^{n+}(\operatorname{ClO}_{4}^{-})_{n} + ne^{-}$$
(1)

To incorporate the anions within the PtPc film, electronically conducting pathways within the microcrystals have to be nucleated. The formation of these pathways follows a nucleation/growth type mechanism in which the PtPc film undergoes a phase transformation.

4.1. Molecular changes in the PtPc films during voltammetry

Many kinds of MPc have rod-like crystallites with a width of about 20 nm, evidenced by SEM images [31], and XRD patterns of the MPc films exhibiting a single sharp peak, indicating that MPc molecules are aligned in crystal grains. Great advances have been made in modifying the structure of phthalocyanine molecular conductive materials by using counterions other than halides [1]. Anions can take part in self-assembly and distribute evenly along segregated closely arrayed stacks of the cationic MPc. The resulting structure depends upon many factors — for instance the level of partial oxidation of the phthalocyanine. A partially oxidised PtPc(ClO₄)_{0.5} crystal was reported to be composed of molecular columns piled up along the c-axis with anions located at the interlayer positions [14]. Since the diameter of ClO_4^- is larger than half the c-axis, the anions and voids should be located alternately along the *c*-axis.

The first voltammetric cycle is special, as during this process anions are irreversibly inserted into the PtPc film structure leading to a discrepancy in the cathodic/ anodic charge balance, Table 1. During the first scan, the process responsible for peak 1 does not occur appreciably until after the start of peak 2. As will be described below, peak 2 corresponds to the nucleation and growth of a new phase, and concomitant with this is an increase in the conductivity of the film. It thus seems likely that the delayed onset of peak 1 is due to

the initial low conductivity of the freshly prepared film. Subsequent voltammetric scans are of a film which retains considerable amounts of anions and which shows much higher conductivity, resulting in a shift of peak 1 to lower potentials. Subsequent discussion will be confined to such pre-conditioned films.

A PtPc crystal grain seems to have a number of interlayer positions of different sizes. Some of them are large enough to directly accommodate anions. The anions can enter and leave these positions easily. Some sites are not sufficiently large to accept the anions, but they can become large enough to accommodate them after a phase transformation. Others are too small and it is difficult for them to grow larger through a phase transformation of the material. Dimensional changes in the *c*-axis direction are possible for the rod-like MPc, resulting in a change of interlayer distance. Chain-direction dimensional changes are observed in the doping/undoping process of various polymers [43-45]. This might be used to explain the reversible phase transformations and the size effect of the anions. When the PtPc microcrystals are oxidised in the region of peak 1, anions enter the microcrystals and occupy some of the large interlayer positions. During this process there is no structural change in the crystals. When an overpotential is large enough to initiate the phase transformation, the microcrystals swell to produce more large interlayer positions that are occupied by a certain amount of the anions at the potential of peak 2. At even higher potentials, the repulsive interactions between the charged columns increase and the microcrystals will undergo another phase transformation resulting in more anions being taken up. During the reverse process, the repulsive interactions between the columns decrease. The microcrystals will gradually recover their original structure, during which process the intercalated anions are expelled.

Some authors reported that polarization of polypyrrole films at high cathodic potentials leads not only to the reduction of the polymer but also to conformational changes in the structure which results in a highly compact film [46,47]. Reoxidation of the film is thus controlled by the conformational relaxation process (i.e. swelling of the polymer by solvent), and a dependence of the potential of peak oxidation current is seen with cathodic pre-treatment potential. This phenomenon has not been observed in the PtPc system [24], and so the re-reduced PtPc has a stable structure independent of the cathodic potential.

4.2. Phase transformation of the PtPc film under nucleation/growth kinetics

There are three pieces of evidence, which point to a nucleation and growth mechanism during the electrochemical oxidations occurring at peaks 2 and 3. Firstly, the current–voltage curve has steeper gradients at low scan rates than at high scan rates. This is a tell-tale sign of nucleation and growth [48].

Secondly, the most important feature of the CV is the very large potential difference between the anodic peak and its corresponding cathodic peak. Such large difference can not be explained as electrochemical irreversibility, as the scan rate has no obvious effect on the peak potential. Kogan et al. reported this large peak potential difference for single crystal PtPc electrode in 0.1 mol dm⁻³ TBAPF₆-propylene carbonate solution [12]. They introduced two models. One is based on an N-shaped free energy dependence of the doped system giving rise to a hysteresis-like behaviour [49]. In this case the chemical composition of $PtPc(ClO_4)_x$ can not be continuously controlled by electrochemical doping as the intermediate compositions are not stable. Another proposal to explain the large potential difference involves the introduction of a percolation threshold potential [27], at which the electronic connection between the conducting crystals generates a well-coupled conductive network. An alternative proposal, put forward by Bond et al. in their study of TCNQ is that the high specific interfacial free energy between the two interconverting solid phases (hundreds of mJ cm $^{-2}$) plays a critical part in determining the nucleation rate as a function of overpotential [23]. There analysis shows that for reasonable values of the surface free energy, there exists a critical overpotential, below which the rate of nucleation is vanishingly small, and the system is inert.

Finally, the relation between the peak current and the scan rate is diagnostic of nucleation and growth kinetics. The experimental dependence of I_p on v for several known cases of nucleation/growth is of the form [48]

$$I_{\rm p} \propto v^{\rm X}$$
 (2)

where x is dependent upon the precise nature of the nucleation/growth kinetics and may even depend upon the scan rate [50,51]. In this case, an $I_{\rm p} \propto v^{0.7-0.8}$ linear relationship rules out the possibility of diffusion-controlled or adsorption-controlled kinetics, as usually seen in electrochemical systems.

Based upon the above analysis we ascribe both the peaks 2 and 3 to electrochemical phase transformations which are governed by nucleation/growth kinetics. As peak 2 has a lower overpotential and a smaller halfheight width, the PtPc film at this point shows a smaller hindrance to the phase transformations and a higher rate. Kogan et al. explained the large peak potential difference on the basis of a steric barrier [13]. Crystals within the film consist of two regions. One is the core region in which MPc molecules align compactly with each other; the other is the surrounding region where the molecules align rather poorly [31]. The reversible process is the result of the unimpeded movement of anions into and out of the non-aligned regions at the boundaries of MPc crystals. On the other hand, the irreversible process results from the anions entering the core regions of a crystal grain driven by a rather large overpotential, where they remain even after re-reduction. The two oxidation peaks of CuPc are explained based on this model. But the reversible phase transformations of PtPc microcrystals are difficult to explain using this model especially the voltammetric response at peaks 3 and 5 and the anion size effects.

In order to describe the nucleation and growth process, it is necessary to determine the rate-controlling step. If the formation and growth of nuclei are the rate-controlling step, the current-time transient should be independent of the anion concentration. However, the experiments show that the concentration of $\text{ClO}_4^$ in the electrolyte has a large influence on the currenttime transients. Low concentrations of anion lead to lower transient currents and a longer relaxation time [24]. This dependence indicates that the diffusion of ClO_4^- may be the rate-controlling step, supported by the $t^{-1/2}$ dependence of current at long time. According to the Cottrell equation

$$I = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}}$$
(3)

The slope (K) of $I \sim t^{-1/2}$ line should have the following form

$$K = \frac{nFACD^{1/2}}{\pi^{1/2}}$$
(4)

K should be proportional to C according to this equation. However, the slope has no such relation with C in the experiments. This indicates that the diffusion of ClO_4^- in the solution as the rate-controlling step can be ruled out, and that the diffusion of ClO_4^- in the solid film must be the rate-controlling step.

Because the current-time transient is similar to that caused by the adsorption of organics, it can be assumed that the individual diffusion zones soon disappear after a large number of very small nuclei are formed. Under such conditions the rate of growth is controlled by planar diffusion perpendicular to the surface. The expression assuming a linear isotherm is [52]

$$I = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}} - \left\{ \frac{nFA^2C^2D}{m} \exp\left(\frac{-nF\eta}{RT}\right) \exp\left[\frac{A^2C^2Dt}{m^2} \exp\left(\frac{-2nF\eta}{RT}\right)\right] \exp\left[\frac{ACD^{1/2}t^{1/2}}{m} \exp\left(\frac{-nF\eta}{RT}\right)\right] \right\}$$
(5)

where m is the number of moles in a monolayer of area, A. In this case the diffusion coefficient, D, and the concentration, C, correspond to those of the anion within the film, and not in solution. Although one could attempt to use Eq. (5) to fit the transients, the large number of unknown parameters means that one would have to assume values for some of them. This equation is simplified to the following when the whole of the surface appears to be active to anions approaching the surface:

$$I = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}} \left[1 - \exp\left(\frac{-nF\eta}{RT}\right) \right]$$
(6)

This equation reduces to the Cottrell equation for large η . Thus the appearance of a dependence of current with $t^{-1/2}$ at long time supports the conclusion that diffusion within the film is the limiting factor during oxidation of the film. Under such conditions, inductive loops are not expected to occur during voltammetric cycling when the scan direction is reversed within the potential range at which *PtPc* oxidation occurs.

4.3. Pseudo-capacitance of the partially oxidised PtPc film

The large capacitance effect revealed clearly in Fig. 3 between 0.8 and 1.0 V is an established effect in the doping process of polypyrrole and etherocyclic polymers [53,54]. The related capacitance $C_{\rm L}$ can be obtained from the voltammetric response by simple calculations based on the expression

$$C_{\rm L} = I/\nu \tag{7}$$

where v is the scan rate and I the double layer current, $C_{\rm L}$ is found to reach 8 mF cm⁻² within this potential range. This capacitance is referred to as the redox capacity in conductive polymers and redox polymers [55], and indicates that the oxidised PtPc microcrystals have the ability to store charge. The origin of such large capacitances in polymer electrodes has been discussed in detail by Mermillod and Tanguy and is explained on the basis of charge saturation effects which take place at the end of the doping processes [56,57]. Both faradaic and capacitative currents can be associated with these processes, and in effect the oxidation reaction is completed within this potential range. The large value of the related capacitance can be considered to arise from a double-layer model in which weakly trapped ions are held near surface of piled molecular columns.

5. Conclusions

The following conclusions can be drawn on the basis of the results discussed.

(1) The mechanical abrasion of PtPc microcrystals can be used to deposit material onto inert electrically conductive substrates, and that this technique is especially useful for studying these materials which are insoluble in aqueous and non-aqueous media. The transfer of microcrystals is simple, it can avoid contamination, and avoids the use of a binder. The abrasion only affects minor physical properties of the microcrystals.

(2) The oxidation and reduction of PtPc microcrystals undergo two reversible solid-solid phase transformations, independent of the electrode substrate. Anions have some influence on the process of phase transformation. The reversible transformations imply that PtPc microcrystals may be applied to molecular metal artificial muscles.

(3) Like other conductive polymers, an obvious firstscan effect, large capacitance behaviour upon oxidation and the dependence of conductivity on the potential are observed. Partially oxidized PtPc microcrystals have the ability to store charge and have high conductivity.

(4) The size of the anions limits their ability to enter the microcrystals and thereby limits the rate and extent of oxidation of the microcrystals.

(5) The nucleation and growth process is controlled by the diffusion of anions within the microcrystal.

Acknowledgements

We thank Dr Long and Mr Mongay-Batalla for providing the PtPc samples. We thank Dr Karol Senkiw for performing the XPS work. This project has been funded by the United Kingdom Engineering and Physical Sciences Research Council, Grant GR/L 57920, with support from Johnson Matthey Plc.

References

- [1] T.J. Marks, Angew. Chem. Int. Ed. Engl. 29 (1990) 857.
- [2] R.J. Mortimer, Electrochim. Acta 44 (1999) 2971.
- [3] G.C.S. Collins, D.J. Schiffrin, J. Electrochem. Soc. 132 (1985) 1835.
- [4] M. Kimura, T. Horai, K. Hanabusa, H. Shirai, Chem. Lett. 7 (1997) 653.
- [5] G. Guilloud, J. Simon, Chem. Phys. Lett. 219 (1994) 123.
- [6] M.M. Nicholson, Ind. Eng. Chem. Prod. Res. Div. 21 (1982) 261.
- [7] J. Zagal, R.K. Sen, E. Yeager, J. Electroanal. Chem. 83 (1977) 207.
- [8] C. Coutanceau, P. Crouigneau, J.M. Leger, C. Lamy, J. Electroanal. Chem. 379 (1994) 389.
- [9] J.A.R. Van Veen, C. Visser, Electrochim. Acta 24 (1979) 921.
- [10] A.B.P. Lever, E.R. Milaeva, G.P. Speier, in: C.C. Leznoff, A.B.P. Lever (Eds.), Phthalocyanines: Properties and Applications, vol. 3, VCH, New York, 1993, p. 1.

- [11] C. Paliteiro, A. Hamnett, J.B. Goodenough, J. Electroanal. Chem. 239 (1988) 273.
- [12] I.L. Kogan, K. Yakushi, Electrochim. Acta 43 (1998) 2053.
- [13] I.L. Kogan, K. Yakushi, J. Mater. Chem. 7 (11) (1997) 2231.
- [14] H. Yamakado, K. Yakushi, N. Kosugi, H. Kuroda, A. Kawamoto, J. Tanaka, T. Sugana, M. Kinoshita, S. Hino, Bull. Chem. Soc. Jpn. 62 (1989) 2267.
- [15] A.K. Shukla, C. Paliteiro, R. Manoharan, A. Hamnett, J.B. Goodenough, J. Appl. Electrochem. 19 (1989) 105.
- [16] C. Paliteiro, A. Hamnett, J.B. Goodenough, J. Electroanal. Chem. 249 (1988) 167.
- [17] C. Paliteiro, A. Hamnett, J.B. Goodenough, J. Electroanal. Chem. 160 (1984) 359.
- [18] R.H. Campbell, G.A. Heath, E.T. Hefter, R.C.S. Mc-Queen, J. Chem. Soc. Chem. Comm. (1983) 1123.
- [19] F. Scholz, B. Meyer, in: A.J. Bard, I. Rubenstein (Eds.), Electroanalytical Chemistry, vol. 20, Marcel Dekker, New York, 1998, pp. 1–86.
- [20] M. Whalley, J. Chem. Soc. (1961) 866.
- [21] C.J. Brown, J. Chem. Soc. A (1968) 2494.
- [22] M. Ashida, N. Uyeda, E. Suito, Bull. Chem. Soc. Jpn. 39 (1966) 2616.
- [23] A.M. Bond, S. Fletcher, P.G. Symons, Analyst 123 (1998) 1891.
- [24] J. Jiang, A. Kucernak, unpublished results.
- [25] M. Kalaji, L.M. Peter, L.M. Abrantes, J.C. Mesquita, J. Electroanal. Chem. 274 (1989) 289.
- [26] M. Kalaji, L. Nyholm, L.M. Peter, J. Electroanal. Chem. 313 (1991) 271.
- [27] K. Aoki, M. Kawase, J. Electroanal. Chem. 377 (1994) 125.
- [28] W.J. Albery, Z. Chen, B.R. Horrocks, A.R. Mount, P.T. Wilson, D. Bloor, A.T. Monkman, C.M. Elliott, Faraday Discuss. Chem. Soc. 88 (1989) 247.
- [29] T.M. Green, L.R. Faulkner, J. Am. Chem. Soc. 105 (1983) 2950.
- [30] J.L. Kahl, L.R. Faulkner, K. Dwarakanath, H. Tachikawa, J. Am. Chem. Soc. 108 (1986) 5434.
- [31] N. Toshiwa, T. Tominaga, S. Kawamura, Bull. Chem. Soc. Jpn. 69 (1996) 245.
- [32] R.L. Kay, B.J. Hales, G.P. Cunningham, J. Phys. Chem. 71 (1967) 3925.
- [33] H.Y. Yeager, B. Kratochvil, J. Phys. Chem. 75 (1969) 1963.
- [34] V. Peulon, G. Barbey, J.J. Makindain, Synth. Met. 82 (1996) 111.
- [35] G. Inzelt, G. Horanyi, Electrochim. Acta 35 (1990) 27.
- [36] J. Barthel, W. Kunz, J. Solution Chem. 17 (1988) 399.
- [37] T. Yea, K.M. Yin, J. Carbajal, R.E. White, J. Electrochem. Soc. 138 (1991) 2869.
- [38] T.F. Otero, E. Angulo, Solid State Ionics 63–65 (1993) 803.
- [39] T.F. Otero, H. Grande, J. Rodriguez, J. Electroanal. Chem. 394 (1995) 211.
- [40] S. Fletcher, J. Electroanal. Chem. 164 (1984) 11.
- [41] V.I. Gavrilov, N.V. Butusova, E.A. Luk'yanets, I.V. Shelepin, Electrokhimiya 16 (1980) 1320.
- [42] V.I. Gavrilov, L.G. Tomilova, I.V. Shelepin, E.A. Luk'yanets, Electrokhimiya 15 (1979) 914.
- [43] R.H. Baughman, Synth. Met. 78 (1996) 339.

- [44] K. Kertesz, F. Vonderviszt, S. Pekker, Chem. Phys. Lett. 90 (1987) 430.
- [45] R.H. Baughman, N.S. Murthy, H. Eckhardt, M. Kertesz, Phys. Rev. B 46 (1992) 10515.
- [46] T.F. Otero, H. Grande, J. Rodriquez, J. Phys. Chem. B 101 (1997) 8625.
- [47] C. Odin, M. Nechtschein, Phys. Rev. Lett. 67 (1991) 1114.
- [48] S. Fletcher, C.S. Halliday, D. Gates, M. Westcott, T. Lwin, G. Nelson, J. Electroanal. Chem. 159 (1983) 267.
- [49] S.W. Feldberg, I. Rubinstein, J. Electroanal. Chem. 240 (1988) 1.
- [50] E. Bosco, S.K. Rangarajan, J. Chem. Soc. Faraday Trans. 1 (77) (1981) 483.

- [51] S.K. Rrangarajan, Faraday Symp. Chem. 12 (1989) 103.[52] R.D. Armstrong, J.A. Harrison, J. Electrochem. Soc. 116
- (1969) 328.[53] S. Panero, P. Prosperi, S. Passerini, B. Scrosati, D.D. Perlmutter, J. Electrochem. Soc. 136 (1989) 3729.
- [54] T.B. Hunter, S. Tyler, W.H. Smyrl, H.S. White, J. Electrochem. Soc. 134 (1987) 2198.
- [55] C.E.D. Chidsey, R.W. Murray, J. Phys. Chem. 90 (1986) 1479.
- [56] N. Mermillod, J. Tanguy, F. Petiot, J. Electrochem. Soc. 133 (1986) 1073.
- [57] J. Tanguy, N. Marmillod, M. Hoclet, J. Electrochem. Soc. 134 (1987) 795.