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ELECTROCHROMISM IN PRUSSIAN BLUE

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SUMMARY

Prussian blue (PB) has been electrodeposited on ITO-glass coated electrode. Electrochromism effect, stability of the film against continued ciclation of potential and influence of nitrate and chloride ions has been studied.

INTRODUCTION

As well-known, PB (Ferric Ferrocyanide) is an important member of the family of metal hexacyanometalates. In the past few years, interest in these mixed-valency compounds was renewed due to the easiness for coating it as thin-films on electrodes (1-4), allowing its use in electrochromic devices (5-7). The deposition can be carry out chemically (1-3) or electrochemically (1, 2) on different substrates: Pt (1-3), glassy Carbon (2), Au (2, 3) or transparent electrodes like ITO (Indium Tin Oxide) (4) and FTO (Fluorine Tin Oxide) (6).

PB has been described in two different formulas: soluble PB $KFe^{III}[Fe^{II}(CN)_6]$ and insoluble PB $Fe^{III}_4[Fe^{II}(CN)_6]_3$, owing the

names to the peptization ability rather than real solubility.

PB thin-films could give different colors. By applying a cathodic potential, the film is reduced to the colorless Prussian white (Everitt's Salt) and the aplication of anodic one, oxides the PB to Prussian Yellow.

According with Itaya and co-workers (2) for insoluble PB the reactions are formulated by the equations:

$$Fe^{III}_4[Fe^{II}(CN)_6]_3 + 4K^+ + 4e \rightleftharpoons K_4Fe^{II}_4[Fe^{II}(CN)_6]_3 \qquad (I)$$
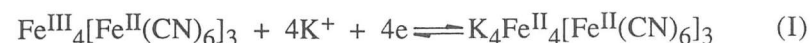
for the reduction equilibrium, and

$$Fe^{III}_4[Fe^{II}(CN)_6]_3 + 3Cl^- \rightleftharpoons Fe^{III}_4[Fe^{III}(CN)_6]_3Cl_3 + 3e \qquad (II)$$

for the oxidation equilibrium.

The aim of this paper is the voltammetric study of different thickness films of PB and compare the effect of nitrate and chloride ions in the destruction of these films on ITO electrodes.

EXPERIMENTAL

Electrochemical experiments were conducted with a Belport HQ Instruments potentiostat and wave generator, equipped with a F-35 Riken Denshi recorder. To observe the film morfology a JEOL JSM-25S Scanning Microscope was used. Visible Spectra was recorded in a Varian, Cary 219 Spectrophotometer. ITO-glass coated was obtained with the reactive sputtering technique. Transmission and refletion

spectroscopies were used to check the optical properties of ITO-glass coated and the film thickness and optical gap were determined. These ITO coatings, deposited with reactive sputtering in air-atmosphere, are highly transparent in the visible region. The equation $d = (\lambda x\lambda')/(2xn(\lambda - \lambda')$ was used to measure the thickness, d, of the ITO film. λ and λ', are the consecutive minimum reflectivity values and n is the real part of the refractive index. To obtain the refractive index of the ITO films in the visible region, the corrected theoric transmittance from the zero absorption is adjusted to the experimental values in the negligible absorption range (5500 Å $\leq \lambda \leq$ 7000 Å) and a linear correlation with refractive index is obtained

$$n = 2.15 - 3x10^{-5} (\lambda(Å) -3000)$$

The direct gap value was obtained by plotting the square absorption cofficient, α^2, against the foton energy. In this way a value gap of 3,8 eV is obtained, that is in agreement with intrinsic In_2O_3 gap (8).

ITO films were obtained from an iron cathode covered with Indium (Aldrich) with 5% Tin content (mass relation).

The potential and current values were adjusted to 2000 ± 50 V and 125 ± 10 mA respectively. The work pressure was 0.12 ± 0.05 torr, the temperature, T = 245°C and the distance cathode/glass was 52 ± 1 mm. In this way, a thickness of 2200 ± 50 Å was obtained.

pH and potentiometric measurements have been carried out with a Radiometer PHM 62 Standard pH - meter. The Reference Electrode was Ag/AgCl(KCl, sat).

PB films were electrochemically deposited on ITO by means of galvanostatic conditions. The ITO - glass (1 cm^2) was immersed in a freshly prepared solution of $FeCl_3$, 0.02 M; $K_3[Fe(CN)_6]$, 0.02 M and KCl, 0.05 M. pH was adjusted to 4.0 with HCl acid. Two types of films
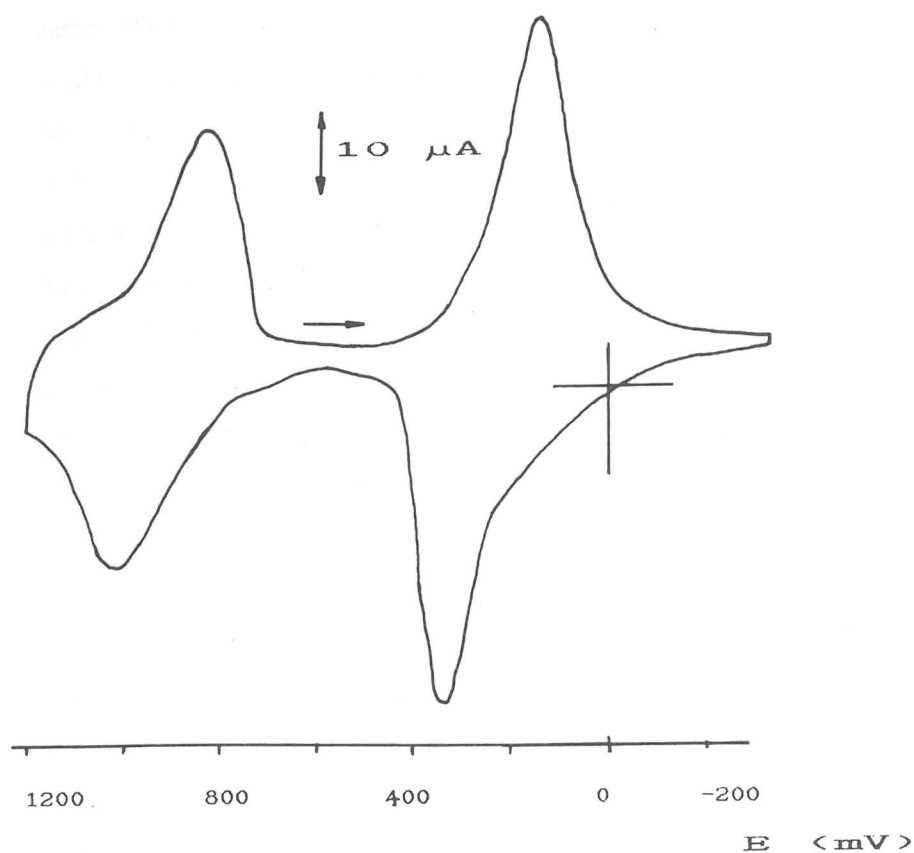
Fig.1.- Cyclic voltammograms of PB in 1 M KCl media. RE: Ag/AgCl(KCl, sat.); CE: Pt; pH = 4.0; T = 20°C; v = 20 mV.s^{-1}. Two redox systems are shown.

were obtained, at 1 minute and three minutes of deposition time. Films were, finally, rinsed with deionized water, methanol and CCl_4 and air-dried.

KCl (Aldrich), $FeCl_3$ (Panreac) were reagent grade. $K_3[Fe(CN)_6]$ was chemically pure. Water has been distilled and afterwards passed through a Milli Q - plus (Millipore) deionizer up to the limit of resistivity of 18 MΩ.cm.

RESULTS AND DISCUSSION

SEM observation of film morphology shows good homogeneity. In similar deposition conditions, Murray et al. (1), by EDX, and Itaya et al.(2), by ESCA, show the absence of K^+ in the as-grown films, i.e. the electrogenerated specie is the insoluble PB.

Cyclic voltammograms show two redox equilibria (Fig. 1): the cathodic one, centered round 240 mV vs Ag/AgCl show greater peaks, and the anodic one, centered round 870 mV shows signals with lower peak currents. In KCl media, cyclation round the anodic system produces film bleaching and quick decrease in the peak height (Fig. 2).

The calculated $n\alpha_a \cong n\alpha_c \cong 0.5$ (Table I) values from these peaks with the aproximated equation (9)

$$n\alpha = 47.7/(E_p - E_p/2)$$

corresponds to an electrochemically irreversible system.

The apparent irreversibility is due to the overall process complexity. The faradaic process and the film destruction occur together. The apparent irreversibility is greater in the first anodic scan ($n\alpha_a = 0.32$) than in the cathodic one ($n\alpha_c = 0.45$) (Table II), so the
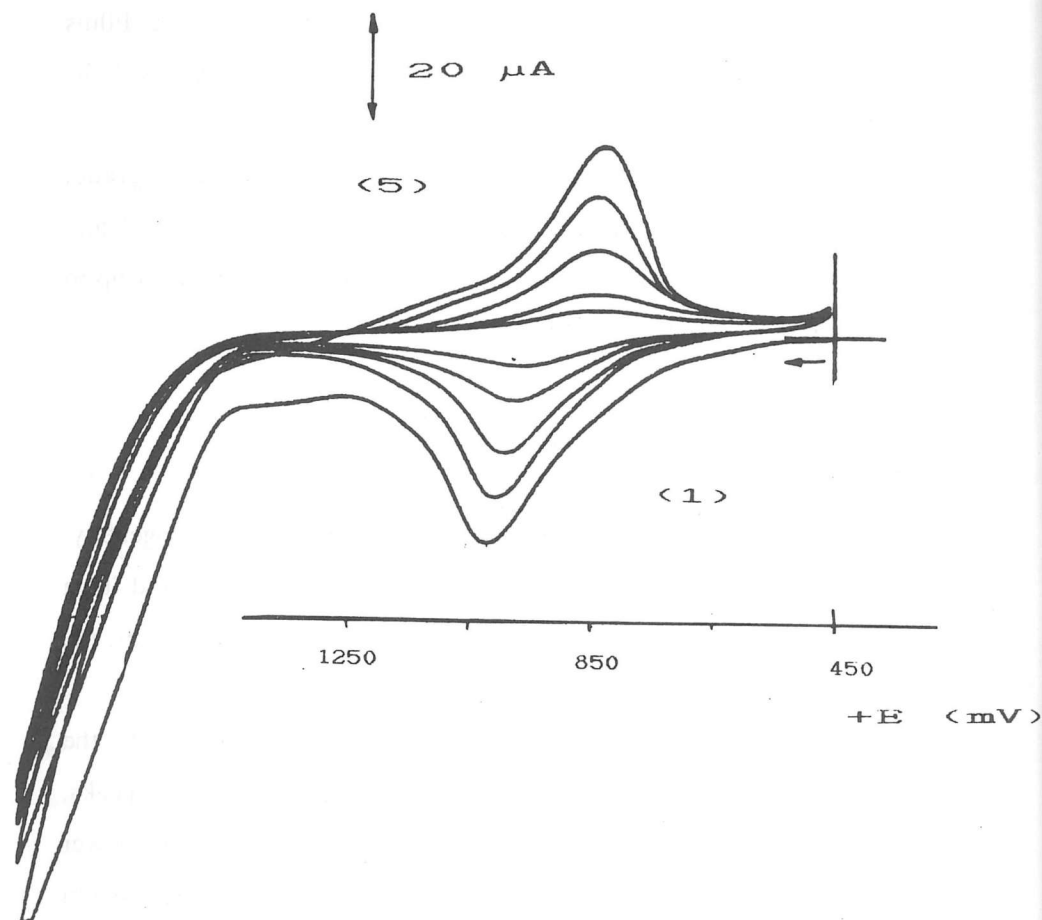
Fig.2.- Cyclic voltammograms of PB in 1 M KCl media. Film destruction with consecutive cycles, round +870 mV, is shown RE: Ag/AgCl(KCl, sat.); CE: Pt; pH = 4.0; T = 20°C; v = 20 mV.s⁻¹.
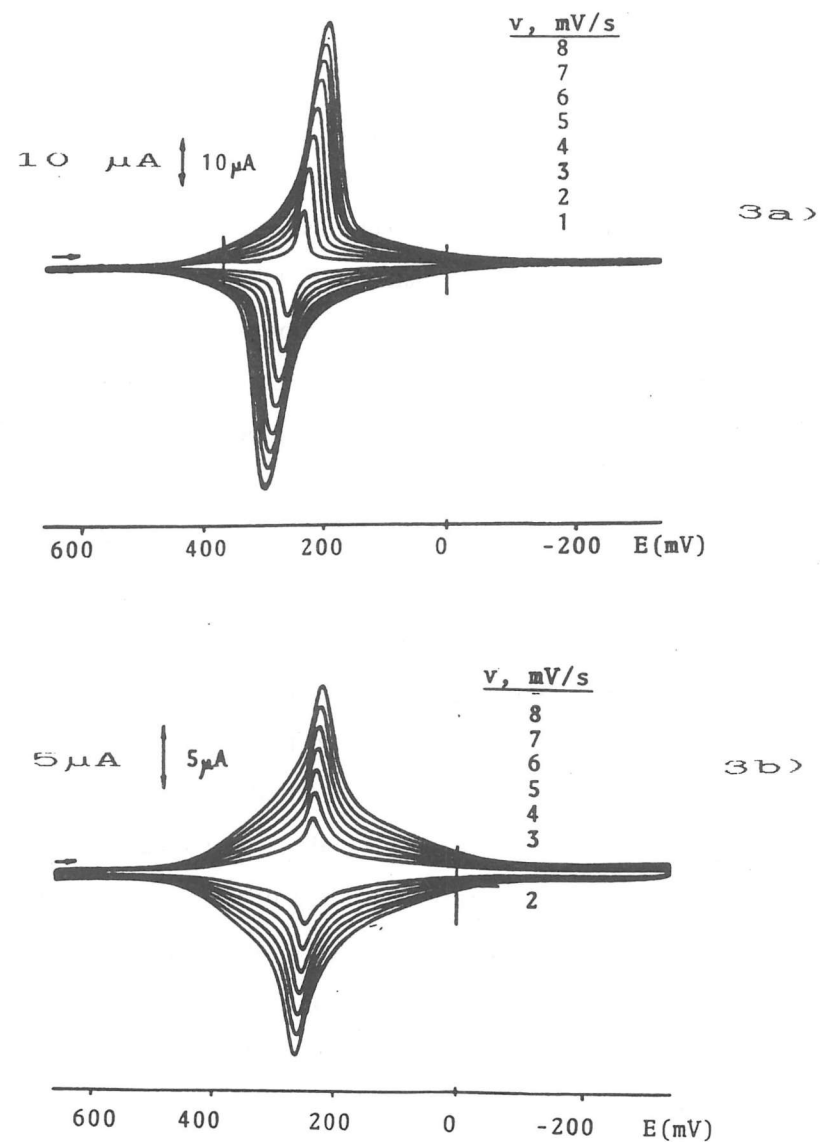

Fig.3.- Cyclic voltammograms of PB thin films in 1 M KCl media with: a) three minutes of deposition time, t_d, and b) one min. of t_d. RE: Ag/AgCl(KCl, sat.); CE: Pt; pH = 4.0; T = 20°C. Dependence on scan speed, v is shown.

film breaking starts with the oxidation peak, when the Cl$^-$ ions attack the PB structure according to process (II). This fact is in agreement with peak current values $i_p^a > i_p^c$. The fast decreasing in the peak current (i_p^a and i_p^c) values with consecutive cycles, reveals the PB film breaking and removal from the ITO-glass surface (Fig. 2). On the other hand, the more markedly change in E_p^a than in E_p^c, confirms the PB-film destruction in the oxidation reaction of overall process (II). The decrease in the transferred charge in each cycle, again shows the PB removal from the ITO surface and it is a measurement of the film thickness decreasing (Table II)

The system shows memory effect and by applying suitable potentials, colorless, blue, green and yellow states can be obtained. It is noteworthy that ITO remains unaltered in this potential range.

With PB deposited films for 3 minutes of deposition time, t_d, voltammograms (Fig. 3) are recorded in the potential range of the equilibrium PB $\rightleftharpoons$ ES, centered round 240 mV (vs Ag/AgCl). Linear relations between peak currents, i_p^a and i_p^c, and square root of the scan speed, $(v)^{1/2}$, are obtained, revealing diffusive control process (Fig. 4). Anodic and cathodic peak currents are substantially the same in the whole scan speed range while the potential peak separation increases with the scan speed (Table II), revealing the electrochemical reversibility decreasing.

With films of t_d = 1 minute, the voltammograms recorded change in the same way as those obtained for 3 minutes, but graphs of peak currents vs $(v)^{1/2}$ slightly deviate from linearity. This fact, possibly reveals two different transport mechanisms that control the overall process I: transport through solid/liquid interface and transport of ionic species inside the PB film.

In these thinner films, greater electrochemically reversibility is obtained (Table III) due to the less voltage drop inside the film. On the
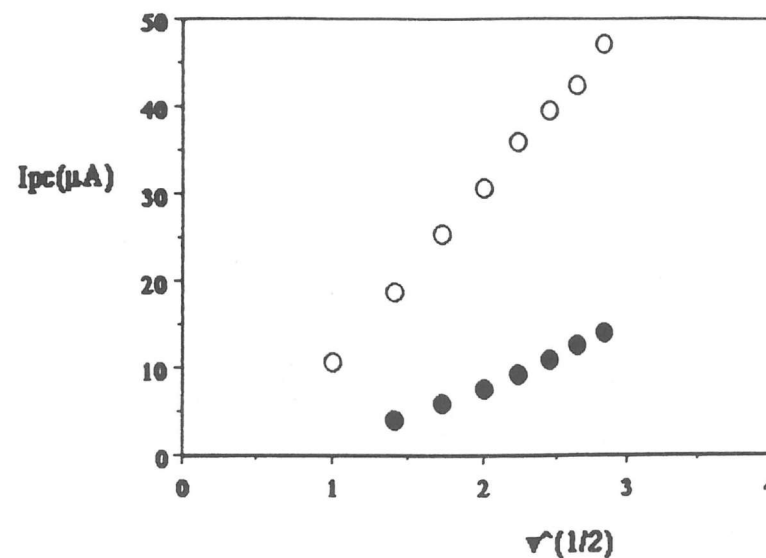
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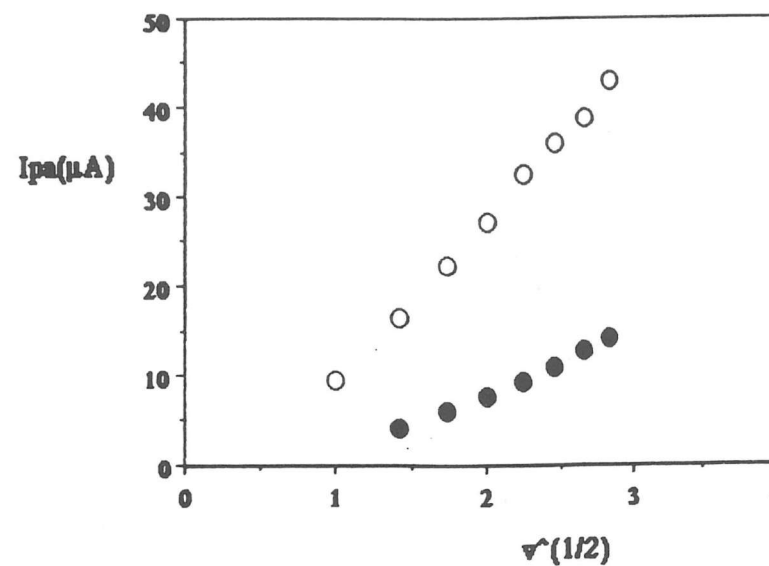
4 b >

Fig.4.- Ip dependence with square root of scan speed, $(v)^{1/2}$.

a) I_p^c. (o): t_d = 3 minutes. (●) td = 1 minute.

b) I_p^a. (o): t_d = 3 minutes. (●) td = 1 minute.

Table I.- Voltammetric parametes variation of PB thin film with consecutive cycling. Ip is given in µA, Ep in mV and Q in mC.

cycle	Ipc	Epc	Qc	$n\alpha_c$	Ipa	Epa	Qa	$n\alpha_a$
1	33.9	830	5.17	.45	38.4	1021	4.70	.32
2	24.9	840	2.96	.45	30.5	1006	3.75	.41
3	14.7	845	1.91	.43	22.0	992	2.74	.45
4	5.7	845	.98	.46	12.4	972	1.66	.45

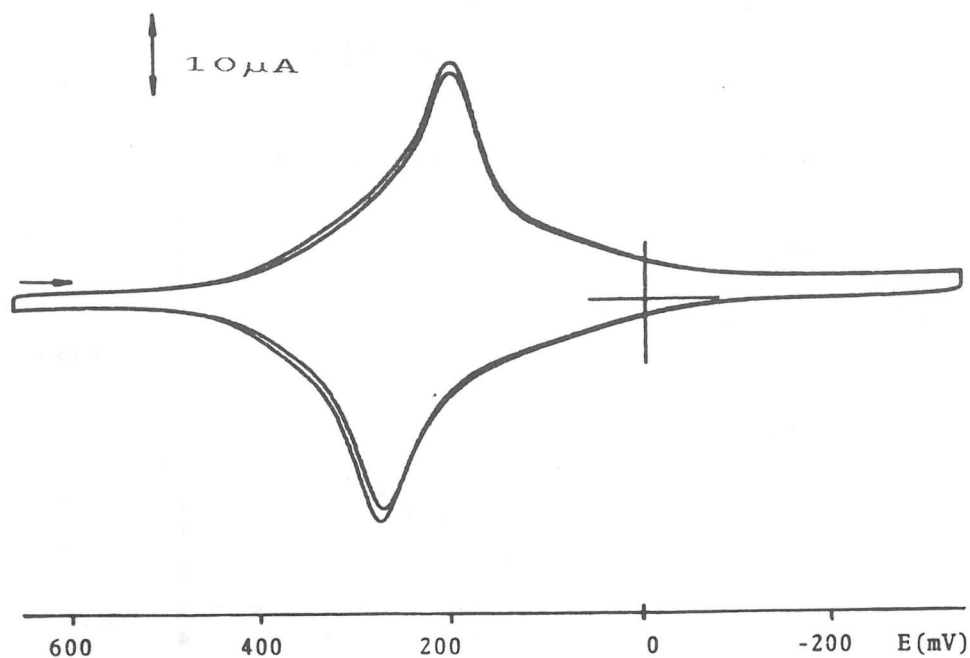
Fig.5.- Two diferent voltammograms of of PB thin film in 1 M KCl media. The system with smaller peaks was recorded after 5 hours of continued cyclation. RE: Ag/AgCl(KCl, sat.); CE: Pt; pH = 4.0; T = 20°C. v = 20 mV.s^{-1}.

Table II.- Dependence of voltammetric parameters of PB thin film (t_d = 3 minutes) on scan speed

v(mV/s)	Ipa(µA)	Ipc(µA)	Epa(mV)	Epc(mV)	ΔE(mV)	$n\alpha_a$	$n\alpha_c$
2	4.1	4.1	245	232	12	1.50	1.54
3	6.0	6.0	250	230	20	1.00	1.59
4	7.7	7.7	250	227	23	1.29	1.33
5	9.4	9.4	255	225	30	1.14	1.11
6	11.0	11.0	255	223	32	1.19	1.06
7	12.7	12.7	260	220	40	1.06	.99
8	14.2	14.2	260	215	45	1.06	.87

Table III.-Dependence of voltammetric parameters of PB thin film (t_d = 1 min) on scan speed

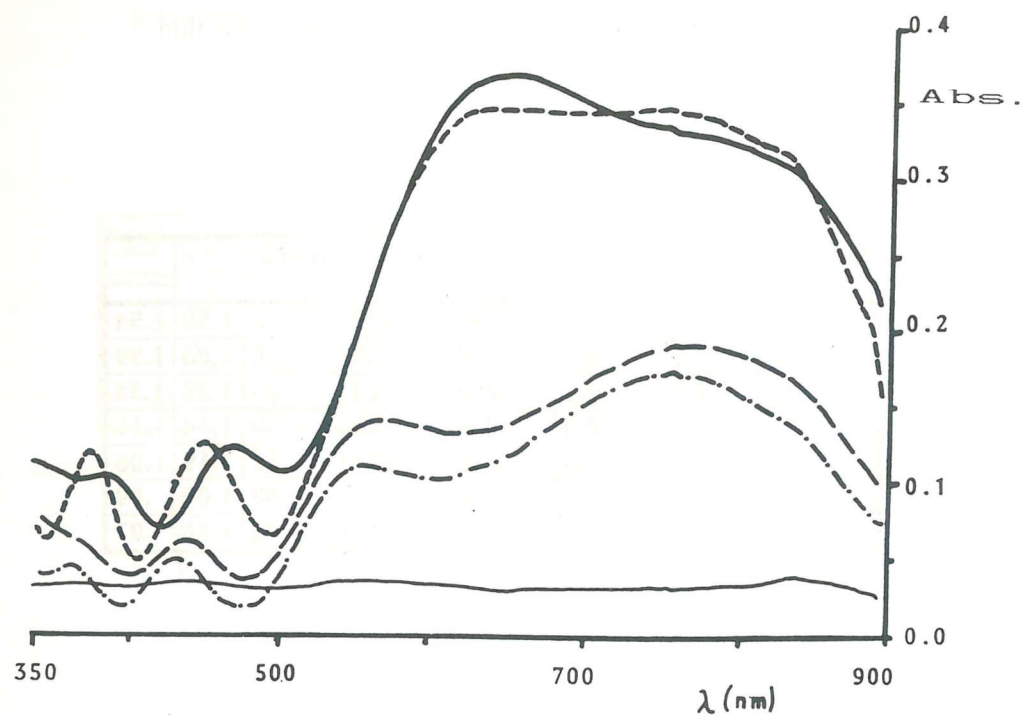| v(mV/s)	Ipa(µA)	Ipc(µA)	Epa(mV)	Epc(mV)	ΔE(mV)	$n\alpha_a$	$n\alpha_c$
1	9.4	10.62	260	232	28	3.95	2.98
2	16.5	18.88	270	223	47	2.39	2.39
3	22.4	25.37	278	212	65	1.70	1.70
4	27.1	30.68	282	208	75	1.65	1.77
5	32.5	35.99	290	200	90	1.29	1.45
6	36.0	39.53	292	195	98	1.29	1.26
7	38.9	42.48	295	192	102	1.19	1.16
8	43.1	47.20	300	188	112	1.06	1.19

Fig.6.- Absorbance spectra for PB films on ITO-glass coated with diferent deposition time.

(——) As-grown film. (t_d = 3 minutes).

(- - -) recorded after cycling process. (t_d = 3 minutes).

(——) As grown film. (t_d = 1 minutes).

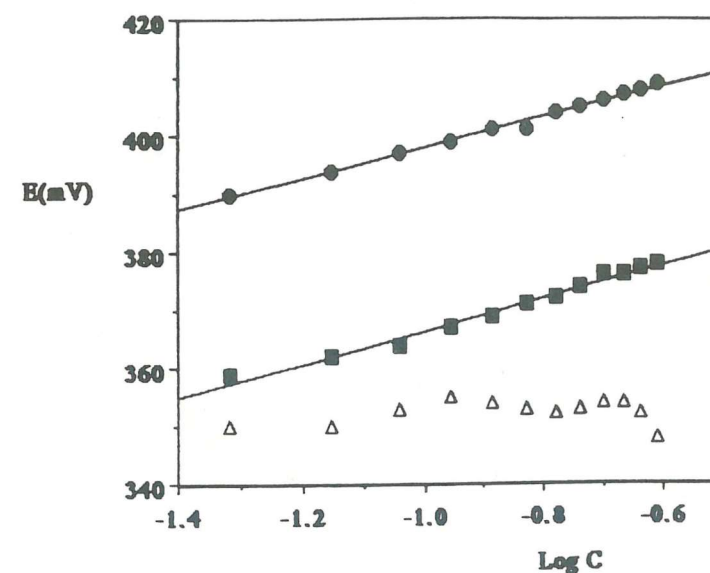(-··-) recorded after cycling process. (t_d = 1 minutes).

Fig.7.- Measured potential of PB film versus Ag/AgCl(KCl, sat.).

Dependence on some ion concentration.

(●) Dependence on KNO_3 concentration.

(■) Dependence on NaCl concentration.

(△) Dependence on $NaNO_3$ concentration.

other hand, the thinner films give smaller peak currents than the thicker ones, aproximatelly one third smaller. Also transferred charge is greater in films with three minutes of deposition time (Table IV).

Continuous cycling for five hours between + 650 mV and - 330 mV potential limits (at a scan speed, v = 20 mV.s^{-1}), produces only 2% of peak height decreasing (Fig. 5), denoting high stability of the film against potential cyclation in KCl medium to study the electrochromic effect in the equilibrium:
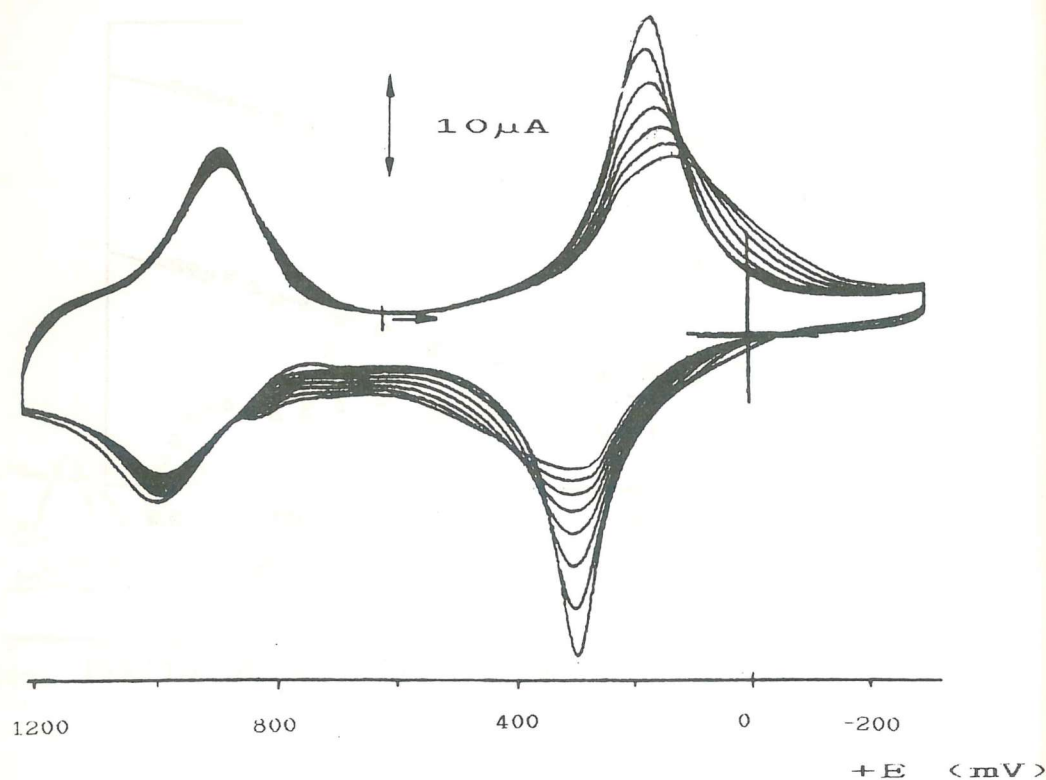
Fig.8.- Voltammograms of PB film (t_d = 3 minutes) in 1 M KCl media. Decreasing of peak current with consecutive cycles is shown. RE: Ag/AgCl(KCl, sat.); CE: Pt; pH = 1.82 T = 20°C. v = 20 mV.s^{-1}.

PB (blue) $\rightleftharpoons$ ES (colorless)

This fact has been checked with visible absorbance spectroscopy by comparing spectra before and after cycling process (Fig. 6).

In accordance with global stoichiometry from process I, to obtain color change, transport of K$^+$ ion from bulk solution to film structure is needed.

The determining roll of K$^+$ ion in the PB reduction has been set

Table IV.-Variation of transferred charge, for process I, with film thickness. For the same thickness, the transferred charge remain pratically constant with scan speed. Anodic and cathodic charge, Qa and Qc are given in mC.

v(mV/s)	Qc(3')	Qa(3')	Qc(1')	Qa(1')
1	5.88	5.32	•	•
2	5.21	5.35	2.14	2.14
3	5.29	5.27	2.29	2.29
4	5.32	5.39	2.31	2.31
5	5.36	5.28	2.28	2.28
6	5.33	5.19	2.32	2.32
7	5.27	5.13	2.37	2.37
8	5.45	5.22	2.42	2.42

3' (film formed during 3 minutes)
1' (film formed during 1 minute)

forth by potentiometry, and are in agreement with the voltammetric studies from other authors. These found that alkaline ions like Li$^+$ and Na$^+$ do not give the electrochromic process, due perhaps, to its solvated ionic size (1-3).

Electrode potential of PB/ITO system against the reference one (using LiClO$_4$ salt bridge), do not vary with the NaNO$_3$ concentration. On the other hand, the variation appear with the K$^+$ and Cl$^-$ concentration increasing (Fig. 7).

The roll of Cl$^-$ ion is fundamental in the overall process II, which gives the color change

PB (blue) $\rightleftharpoons$ PY (yellow)

When the consecutive potential scans are done in KNO_3 (Fig. 8) medium, the decrease in the anodic peak size from process I, PB (blue) $\rightleftharpoons$ ES (colorless) is greater than in the KCl medium. However, Cl^- as well as NO_3^- ions participate in film destruction, since both take part in PB solubilization process during consecutive cycling

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USO DE ELÉCTRODOS SELECTIVOS DE IÕES COMO DETECTORES EM ANÁLISE POR INJECÇÃO EM FLUXO

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RESUMO: Apresenta-se uma revisão crítica dos cerca de 100 artigos que descrevem a utilização de eléctrodos selectivos de iões (ESIs) como detectores em sistemas de análise por injecção em fluxo (FIA), procurando-se fazer uma análise sistemática dessa utilização. Consideram-se sucessivamente os seguintes três aspectos: a inserção de ESIs em sistemas de FIA, as características dos sistemas de FIA em que são utilizados ESIs, e as suas aplicações analíticas.

ABSTRACT: A critical review of the *ca.*. 100 papers in wich ion-selective electrodes (ISEs) are used as detectors in flow-injection analysis (FIA) systems is presented, with the purpose of identifying systematic patterns of utilization. Three points, the insertion of the ISEs in FIA systems, the characteristics of FIA systems in wich ISEs are used, and their analytical applications, are considered in turn.

INTRODUÇÃO

A escolha do tipo de detector tem grande importância nos processos de análise por injecção em fluxo (FIA), uma vez que a sensibilidade e selectividade destes dependem não só das reacções desenvolvidas no sistema de fluxo como também das características do detector. A potenciometria com eléctrodos selectivos de iões (ESIs), apesar de não ser a técnica de detecção mais utilizada em FIA até ao presente, reúne boas características para este fim. Conforme refere Cammann [1], os ESIs apresentam certas vantagens únicas, nomeadamente, entre outras: a técnica potenciométrica é simples e não requer instrumentação dispendiosa; os ESIs podem ser utilizados numa gama bastante ampla de concentrações, em geral de duas a três décadas; em regra, não é necessário recorrer à utilização de um reagente específico, uma vez que os eléctrodos são suficientemente selectivos para efectuar a detecção sem qualquer tratamento prévio; pode-se aumentar a