

ORIGINAL PAPER

Pawel J. Kulesza · Silvia Zamponi · Marcin A. Malik
Krzysztof Miecznikowski · Mario Berrettoni
Roberto Marassi

Spectroelectrochemical identity of Prussian blue films in various electrolytes: comparison of time-derivative voltabsorptometric responses with conventional cyclic voltammetry

Received: 16 January 1997 / Accepted: 11 March 1997

Abstract Using Prussian blue (PB) electrodeposited on gold-covered foil as a model system, we have demonstrated the usefulness of the time-derivative measurements of absorbance versus potential (linear potential-scan voltabsorptometry) for spectroelectrochemical characterization of thin electrochromic films. The time-derivative signals were monitored for PB at 680 and 420 nm in potassium, sodium and lithium electrolytes. Information obtained from cyclic voltabsorptometry is equivalent or complementary to that from conventional cyclic voltammetry. In the case of PB films investigated in lithium electrolyte, the voltabsorptometric time-derivative peaks are better defined than the respective voltammetric peaks. The combination of voltabsorptometry with voltammetry enables molar absorptivity and/or film loading to be determined. Also, concentration changes of differently colored mixed-valence redox centers can be monitored as a function of applied potential.

Key words Prussian blue · Voltabsorptometry · Alkali metal cations · Electrochromism

Introduction

Prussian blue (PB), iron(III) hexacyanoferrate(II) [1, 2], has been an object of intense research in the area of chemically modified electrodes for many years. PB is a

prototype of metal hexacyanoferrates, and belongs to the important class of mixed-valence electron-hopping compounds [3] which typically feature cubic lattices with defects, interstitial sites, and vacancies where counterions can be intercalated [2, 4]. Electrolyte cations, particularly hydrated potassium ions, easily penetrate the PB structure, and their flux provides charge balance during the system's redox reactions [5–8]. The material is sparingly soluble and is capable of forming polymer-like electroactive films on electrode surfaces. PB shows interesting properties which make the system potentially applicable for energy storage [9, 10], ion exchange [11–12], sensors [13] and electrochromic display devices [14–20]. The latter characteristics have merited special attention during recent years because of the good stability and low cost of PB, the electrochemical reversibility of its redox reactions and the possibility of multiple switching from a dark to a transparent state.

It has been established that in aqueous potassium electrolytes, i.e. under conditions where ionic penetration through PB is fast and redox reactions are facile, the system shows reversible electrochromic behavior: it turns colorless (transparent) upon reduction to Everitt's salt, and it becomes yellow or light green (almost transparent) upon oxidation to Prussian yellow or to the mixed form of Berlin green [21, 22]. In this context, PB can be viewed as a model system for spectroelectrochemical studies. In the present work, we evaluate the usefulness of time-derivative voltabsorptometric measurements for the characterization of such electrochromic materials as PB.

Limited and sometimes conflicting information is available on the electrochemical and spectrochemical behavior of PB films in supporting electrolytes containing cations other than potassium ions. It has sometimes been postulated that virtually only potassium can freely penetrate the PB lattice [2], but other workers have observed that protons may replace potassium in acid solutions [23], and that sodium ions can

P.J. Kulesza (✉) · M.A. Malik · K. Miecznikowski
Department of Chemistry, University of Warsaw, Pasteura 1,
PL-02-093 Warsaw, Poland

S. Zamponi · M. Berrettoni · R. Marassi
Dipartimento di Scienze Chimiche, Università di Camerino,
via S. Agostino 1, I-62032 Camerino, Italy

M.A. Malik
Division of General Chemistry, Department of Metallurgy and
Materials Engineering, Technical University of Czestochowa,
Armii Krajowej 19, PL-42-200 Czestochowa, Poland

be inserted into PB and transported within the structure during solid-state voltammetric experiments [24, 25]. We report here on the spectroelectrochemical behavior of PB films in electrolytes containing potassium, sodium, lithium, and hydronium cations. We have deposited PB films on gold-covered foil, since this light-transparent substrate provides good contrast and shows better conductivity than that of indium/tin oxide optically transparent electrodes. We demonstrate the utility of the time-derivative linear potential-scan voltabsorptometric approach [26–28] for the characterization of PB films upon exposure to various supporting electrolytes. We have found that plots of the time derivative of absorbance versus potential not only provide information equivalent to that available from conventional voltammetry, but often yield responses superior to those of the corresponding current signals.

Experimental

Nafion 117, a perfluorinated ion-exchange membrane, was used as a 5 wt% alcoholic solution (from Aldrich). All other chemicals used were of analytical grade and were used as received. Water which was doubly distilled and subsequently deionized was used for the preparation of solutions.

The optically transparent substrates were prepared by the evaporation of gold onto transparency foil (for copiers, PP2500 from 3 M) using the Balzers Union MED 010 sputtering system. Before evaporation, the foil was soaked in ethyl alcohol and subjected to ultrasonic cleaning for 2 h. The optimum thickness of gold was 25 nm, and this value can be considered as a compromise between good conductivity and sufficient transparency to light.

Amel System-5000 (Milan, Italy) and CH Instruments Model 660 (Cordova, Tenn., USA) analyzers were used for electrochemical measurements. All potentials are quoted versus a saturated (KCl) Ag/AgCl electrode. A Hewlett-Packard 8452A diode array spectrophotometer was used together with the Amel System to obtain spectroelectrochemical data and voltabsorptometric responses in the visible range. The spectra were recorded at 2-s intervals, which corresponds to 20-mV steps or 10-mV s⁻¹ scan rate. The spectroelectrochemical cell was manufactured from nylon at the University of Camerino. The design featured a thin layer (ca. 4 mm) of electrolyte that was cylindrical along the optical path.

The preparation of Prussian blue (PB) films on gold-covered foil was by electrodeposition (for 1 min) under potentiostatic conditions at 0.5 V in the solution of 0.01 M FeCl₃ and 0.01 M K₃Fe(CN)₆ (with neither KCl nor HCl electrolyte added). Before electrodeposition, the modification solution was deaerated with prepurified nitrogen for 10 min. As a rule, the film was subjected to ten full potential cycles in the potential range 0.5–0.0 V in 0.5 M K₂SO₄. Following this step, the film was rinsed with water, dried, and coated with Nafion by introducing 5–6 drops of Nafion solution to cover the PB surface uniformly. To allow solvent to evaporate, the samples were left for ca. 5 h under ambient conditions (ca. 20°C). We did not find any influence of the Nafion coating on either the electrochemical or the spectrochemical characteristics of PB, except that the treatment improved the long-term stability of the PB films and led to very reproducible results.

The presence of alkali metal cations (in addition to iron) was verified ex situ by performing the elemental analysis of the films (deposited on graphite foil from Goodfellow, England) using an energy-dispersive X-ray (EDX) analysis probe (Leica-Cambridge Model 360). The results were semiquantitative, but, for the freshly prepared films, indicated the presence of K atoms in excess of what would be expected from the formula KFe[Fe(CN)₆]. Further, following exposure of the film to sodium or lithium electrolyte,

K⁺ ions were exchanged virtually completely with Na⁺ or Li⁺. Each time, the respective film was subjected to three full potential cycles in the investigated range of potentials.

Results and discussion

A typical cyclic voltammetric response of PB film in potassium electrolyte consists of two sets of peaks (Fig. 1A). In view of previous reports [2, 5–8], we explain these two sets of voltammetric peaks in terms of two reversible redox reactions of PB: reduction to iron(II) hexacyanoferrate(II) [Everitt's salt (ES)] and oxidation to Prussian yellow (PY) via the mixed-valence form of Berlin green (BG). We show cyclic voltammograms (Fig. 1A, curves a–e) of PB films whose thicknesses were systematically increased (by multiple electrodepositions in a manner described in the Experimental section). Regardless of the thickness of the film, PB shows a characteristic absorption band with a maximum at about 680 nm (Fig. 1B). Curves a–e in Fig. 1B are consistent with the gradual increase of absorbance with the thickness of the PB film. It can be seen in Fig. 1C that the system's absorbance increases linearly with the increasing loading of PB film (in mol cm⁻²). The latter parameter was estimated from the charge under the oxidation peak (at ca. 0.2 V in Fig. 1A) recorded at a slow scan rate (10 mV s⁻¹). Such estimation was justified because the respective voltammetric peak currents (Fig. 1A) were proportional to scan rates up to at least 30 mV s⁻¹. From the slope of the dependence shown in Fig. 1C, we determined (for PB film at 680 nm) the absorptivity coefficient, 6.6 × 10⁶ cm² mol⁻¹, which translates into the molar absorptivity, 6.6 × 10³ dm³ mol⁻¹ cm⁻¹. On the whole, it is apparent from the data of Fig. 1 that PB is a well-

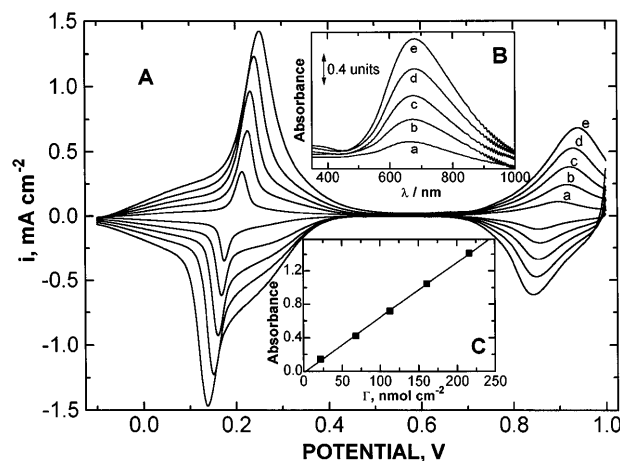


Fig. 1 A Cyclic voltammetric responses of PB films of various thicknesses (film loadings increase from a to e). Scan rate: 10 mV s⁻¹. Inset B shows absorbance spectra of the above PB films (recorded under open circuit conditions). Inset C shows the dependence of absorbance on film loading. Electrolyte: 0.5 mol dm⁻³ K₂SO₄

behaved system suitable for both electrochemical and spectrochemical investigations.

Figure 2 shows the visible spectra of PB films recorded in a spectroelectrochemical cell at 0.550 V in the 0.5 M electrolytes K_2SO_4 , Na_2SO_4 , Li_2SO_4 , and H_2SO_4 . A fresh film (prepared as described in the Experimental section) was generally used for experiments in each electrolyte. Before the actual spectrum was recorded, the PB film was subjected to voltammetric potential cycling (three full cycles) within the potential limits of -0.2 to 1.2 V in the respective electrolyte. EDX analysis showed that such treatment assured almost complete exchange of potassium countercations, initially present in PB, with desired cations. Mechanistically, electrolyte cations are incorporated into PB during reduction cycles [5, 12].

Upon comparison of the curves (Fig. 2), it becomes apparent that the system's major absorption band shifts somewhat toward higher wavelengths following transfers from potassium solutions (680 nm) to sodium (700 nm) and lithium (725 nm) solutions, respectively. The band which is characteristic of a response in the presence of hydronium ions has its maximum at about 700 nm. An attempt has been made to correlate these shifts with the sizes of the hydrated cations [29–31]: K^+ (0.24 nm), Na^+ (0.36 nm) and Li^+ (0.42 nm), as well with the ionic radii of the dehydrated cations [32]: K^+ (0.133 nm), Na^+ (0.095 nm) and Li^+ (0.060 nm). In both cases, systematic changes have been found, although these dependences are in neither case exactly linear. It has been postulated previously for PB and other metal hexacyanoferrates [32–34] that, although alkali metal cations do not retain a complete hydration shell upon entrance to the system's lattice, the actual hydration energies (degrees of hydration) of these countercations decrease in the order $Li^+ > Na^+ > K^+$, analogous to that observed in aqueous solutions. We are unable to offer an unequivocal explanation of the influence of countercations on charge-transfer spectra of PB. Previously, we correlated the color of cobalt(II) hexacyanoferrates with the degree of hydration of interstitial Co(II) ions and with the sys-

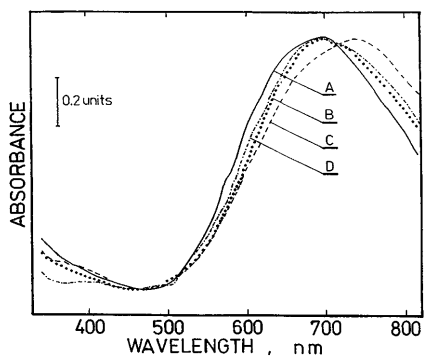


Fig. 2 Absorbance spectra of PB films (held at 0.550 V) recorded in 0.5 M K_2SO_4 (A), Na_2SO_4 (B), Li_2SO_4 (C), and (D) H_2SO_4 . The films were electrodeposited on gold-covered foil. Film loadings $1.7(\pm 0.2) \times 10^{-7}$ mol cm^{-2} , Electrode area 2.5 cm^2

tem's ability to incorporate alkali metal cations of various sizes. This observation may have more general application, since a fundamentally similar, distorted-cubic, structure appears to exist in both PB and related metal hexacyanoferrates [35]. Water molecules are expected to occupy positions about structural Fe(III) where CN ions are missing in PB. The actual aquation of Fe(III) may reflect a contribution from the hydration shell of a countercation sorbed into the PB lattice from supporting electrolyte. It is noteworthy that the changes of the formal potentials of the redox reactions occurring in the films of PB and its analogues can also be correlated with ionic radii of hydrated and dehydrated alkali metal cations [32–34, 36].

Figure 3 shows cyclic voltammograms of PB, deposited on gold-covered foil, which were recorded in various electrolytes. A truly well-defined voltammogram (in the form of two sets of voltammetric peaks) was obtained only by potential cycling in a potassium electrolyte. During the experiments in sodium (curve B) or lithium (curve C) electrolytes, the system's voltammetric responses are much more poorly defined: the peaks are drawn out and significantly lower. It is reasonable to expect a more difficult penetration of the larger hydrated sodium and lithium (in comparison to potassium) cations through the PB lattice [2, 12, 25, 33]. In sulfuric acid solution, the PB film virtually loses its electroactivity. In the presence of hydronium ions, PB may undergo significant structural reorganization. Therefore, acid solutions were not considered further.

We also performed dynamic spectroelectrochemical measurements of PB films in the voltabsorptometric mode. Recently, the theory of linear scan voltammetry within a finite diffusion space has been adopted to describe the responses of linear scan voltabsorptometry [26–28]. Plotting the time derivative of absorbance (of

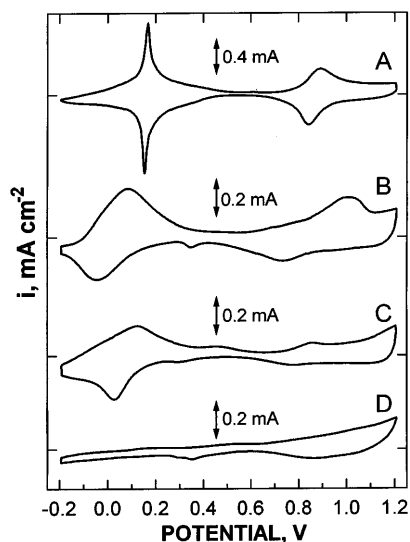


Fig. 3 Cyclic voltammetric responses of PB investigated in 0.5 M K_2SO_4 (A), Na_2SO_4 (B), Li_2SO_4 (C), and H_2SO_4 (D). Scan rate 50 mV s^{-1} . Other conditions as for Fig. 2

colored species participating in an electrode reaction) versus potential has been demonstrated to produce information equivalent to that available from the corresponding conventional voltammogram. Since redox reactions of PB films can also be interpreted in terms of uncomplicated electron transfers occurring in a thin-layer-type system, the peak value of the time (t) derivative signal of absorbance (A), $(dA/dt)_p$, recorded at low (10 mV s^{-1}) scan rate, can be described as follows [27]:

$$(dA/dt)_p = n\epsilon CvdF/4RT = 9.73n\epsilon Cvd \quad (1)$$

where ϵ is the molar absorptivity (in $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), v is a scan rate (in V s^{-1}), C is equivalent to the concentration of redox centers (in mol dm^{-3}), d stands for film thickness (in cm), and other parameters have their usual significance. The coefficient 9.73 has been computed for the temperature of 25°C . It can be shown from Eq. 1 that, for a given PB film and scan rate, the $(dA/dt)_p$ signal would be dependent on the concentration of mixed-valence iron(III,II) or hexacyanoferrate(III,II) centers which are generated in PB during reduction or oxidation, respectively.

In the case of electrodes modified with thin films, it is more convenient to relate the time derivative of absorbance with the loading of a film, Γ (in mol cm^{-2}), rather than with C , i.e. concentration in conventional units (in mol dm^{-3}). Since $C = \Gamma/d$, the following dependence is obtained:

$$(dA/dt)_p = n\epsilon'\Gamma vF/4RT = 9.73n\epsilon'\Gamma v \quad (2)$$

where ϵ' is the absorptivity coefficient (in $\text{cm}^2 \text{ mol}^{-1}$) having the same meaning as ϵ in Eq. 1 except that ϵ' appears in more convenient units. Because Γ can easily be calculated upon estimation of charge under the voltammetric peak recorded in a parallel experiment at a slow scan rate, Eq. 2 permits the determination of ϵ' of the film's material at a selected wavelength. If ϵ' is known, the film loading (Γ) can be found from the voltabsorptometric measurement.

In view of the data of Figs. 1 and 2, the wavelength of 680 nm (maximum absorbance of PB) seems to be the optimum for monitoring $(dA/dt)_p$. We show, in Fig. 4, the time-derivative cyclic voltabsorptograms of

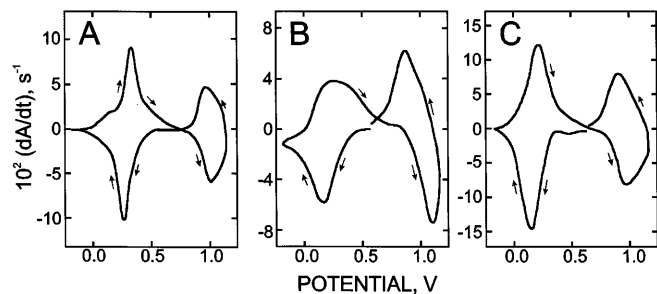


Fig. 4 Time-derivative cyclic voltabsorptograms of PB film recorded at 680 nm in 0.5 M K_2SO_4 (A), Na_2SO_4 (B), and Li_2SO_4 (C). Scan rate, 10 mV s^{-1} . Electrode surface area 2.5 cm^2 . Film loadings $2.1(\pm 0.2) \times 10^{-7} \text{ mol cm}^{-2}$

PB films measured in potassium, sodium and lithium electrolytes. The voltabsorptometric signals at about 0.25 V (Fig. 4) are equivalent to the voltammetric peaks at comparable potentials (Fig. 3). The $(dA/dt)_p$ signals at about 0.9–1.0 V (Fig. 4) are in the opposite direction to the respective voltammetric peaks (Fig. 3) because, during oxidation of PB to Prussian yellow (via Berlin green), the concentration of blue-colored centers decreases. In the presence of sodium ions, the PB voltabsorptometric peaks at ca. 0.25 V (Fig. 4B) are approximately half the size of those recorded in the potassium electrolyte (Fig. 4A). Since both films have almost identical thicknesses (loadings), the result is consistent with the partial “blocking” of PB redox reactions in the sodium electrolyte. The shape of the voltammogram (Fig. 3B) shows that the reduction of PB is less reversible and kinetically complicated in sodium electrolyte than the reduction in potassium electrolyte (Fig. 3A). Consequently, the derivative (dA/dt) values in sodium electrolyte (Fig. 4B) are smaller than those for the fast reaction in potassium electrolyte (Fig. 4A), although the molar absorptivities of PB are practically the same in sodium and potassium electrolytes (Fig. 2). It is noteworthy that Eqs. 1 and 2 have been derived with the assumption that the electrode process is kinetically fast and reversible. In the case of measurements in lithium electrolyte, the voltabsorptometric peaks of PB (Fig. 4C) are much better defined than the distorted, conventional, voltammetric response of the system (Fig. 3C). Voltabsorptometric signals are in a sense “filtered” because they reflect electroactivity of redox centers absorbing only at the selected wavelength. Further, they barely show any background and capacitive contributions [28]. Assuming that $\epsilon' = 6.6 \times 10^6 \text{ cm}^2 \text{ mol}^{-1}$ (as for PB in potassium electrolyte) and using Eq. 2, we have estimated, from a value (0.15 s^{-1}) of the time-derivative absorbance for the PB reduction peak appearing at ca. 0.2 V (Fig. 4C), the film loading, $\Gamma = 2.3 \times 10^{-7} \text{ mol cm}^{-2}$. Such an estimation would be more complex from the distorted cyclic voltammogram of PB in lithium electrolyte (Fig. 3C).

Figure 5 shows changes in the spectral characteristics of PB films during reduction (A) and during oxidation (B and C) in 0.5 M Li_2SO_4 . For simplicity, we present only the data recorded in lithium electrolyte; similar patterns have been found in potassium and sodium electrolytes. It can be seen from Fig. 5A that during reduction of PB, i.e. upon application of potentials from 0.550 down to -0.200 V , the system's characteristic band at about 700 nm decreases (curves a–f), and practically disappears (curve g) following reduction of the film (to Everitt's salt). This result is consistent with the visual bleaching of the film. In the first oxidation cycle starting from -0.200 V (Fig. 5B), the respective band at ca. 700 nm increases (curves a–g) to reach a maximum at 0.850 V (curve h). Such a spectrum corresponds to the blue color of the film. During further oxidation in the potential range from

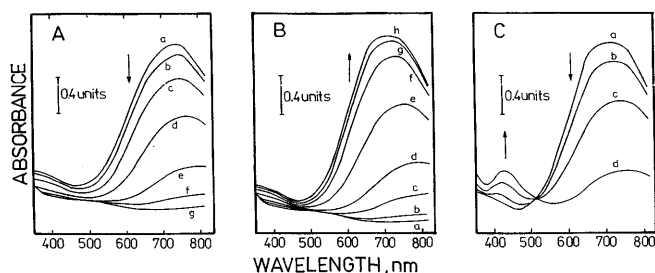


Fig. 5 A–C Spectral changes upon application of the following potentials to the PB film deposited on gold-covered foil. **A** 0.550 V (a), 0.300 V (b), 0.200 V (c), 0.100 V (d), 0.000 V (e), –0.100 V (f), and –0.200 V (g); **B** –0.200 V (a), –0.100 V (b), 0.000 V (c), 0.100 V (d), 0.200 V (e), 0.300 V (f), 0.500 V (g), and 0.850 V (h); and **C** 0.850 V (a), 0.950 V (b), 1.050 V (c), and 1.150 V (d). Electrolyte 0.5 M Li_2SO_4 . Film loading. 2.1×10^{-7} mol cm^{-2}

0.850 to 1.150 V (Fig. 5C), the band at ca. 700 nm decreases (curves a–d), whereas the new absorption band at 420 nm starts to grow. In other words, the fading blue color of the film acquires a yellow component, turns green, and becomes yellow-green at 1.150 V.

The fact that spectral changes in PB occur not only at 680 nm but also at the second band (Fig. 5) has allowed us to perform additional linear sweep voltabsorptometric experiments at 420 nm. Figure 6 summarizes the time-derivative responses of absorbance (at 420 nm) versus potential of PB films recorded in potassium, sodium, and lithium electrolytes. The absorbance at 420 nm is responsible for the yellow-orange coloring component. Therefore, it is not surprising that, in all electrolytes studied, a significant increase of the absorbance at 420 nm has been observed during the oxidation of PB to Prussian yellow (via Berlin green), i.e. at potentials more positive than 0.75 V, when yellow $\text{Fe}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$ centers are generated. Using Eq. 2, we have calculated $\epsilon' = 2.0 \times 10^6$ $\text{cm}^2 \text{mol}^{-1}$. In this estimation, we have accounted for the fact that, in conventional cyclic voltammetry, the charge under the PB systems's oxidation peak is ca. 70% of the charge under its reduction peak.

As expected, the values of (dA/dt) at 420 nm are relatively small at potentials where PB exists. Some attention has been paid to the appearance of small (dA/dt)

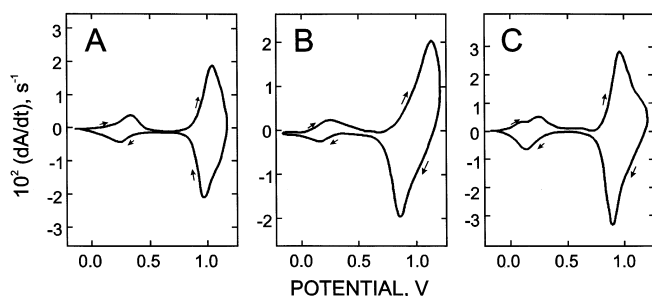


Fig. 6 Time-derivative cyclic voltabsorptograms of PB film recorded at 420 nm. Other conditions as for Fig. 4

(dt) -peaks at potentials 0.20–0.25 V (Fig. 6), where PB is reduced to Prussian white (Everitt's salt). The fact that relatively small amounts of “yellow-colored” redox centers are generated during the reduction of PB may imply some structural inhomogeneity or reorganization, e.g. expulsion of high-spin Fe^{3+} (yellow-orange) ions which are present in the interstitials, during the cycling of the films in potassium solution. Two forms of PB, “soluble” $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ and “insoluble” $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$, are expected to be electrodeposited on electrode surfaces [2]. Redox reactions involving “insoluble” PB may require structural reorganization because stoichiometry of the latter system ($\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$) differs from those of the fully oxidized ($\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$) and reduced ($\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$) forms.

Conclusions

An important feature of the data of Figs. 4 and 6, which show the derivative curves of absorbance versus potential at 680 and 420 nm, respectively, is that the generation of colored mixed-valence centers in PB films can be easily monitored with cyclic voltabsorptometry in (A) potassium, (B) sodium and (C) lithium electrolytes. No reliable data have been obtained in sulfuric acid using either cyclic voltammetry or voltabsorptometry. Voltabsorptometric $(dA/dt)_p$ responses of PB recorded in lithium electrolytes at 680 nm (Fig. 4C) and at 420 nm (Fig. 6C) seem to be much better defined than those in the conventional cyclic voltammogram (Fig. 3C). When combined with conventional voltammetry, linear sweep voltabsorptometry may serve as a good diagnostic tool and may provide structural information. The technique seems to be of importance to the characterization of materials for electrochromic windows and display devices. It is apparent from cyclic, time-derivative voltabsorptometric experiments that PB shows reversible electrochromic behavior not only in a potassium electrolyte but also in a lithium supporting electrolyte.

Acknowledgements We acknowledge the support from the State Committee for Scientific Research (KBN), Poland and MPI, Italy. P. J. K. appreciates a travel grant from University of Camerino. M. A. M. is grateful to the Foundation for Polish Science for a fellowship.

References

1. Sharpe AG (1976) The Chemistry of cyano Complexes of the transition metals. Academic, New York
2. Itaya K, Uchida I, Neff VD (1986) Acc Chem Res 19: 162
3. Brown DB (ed) (1980) Mixed Valence compounds, vol 18. Reidel Dordrecht, NATO Advanced Institute Series
4. Buser HJ, Swarzenbach D, Peter W, Ludi A (1977) Inorg Chem 16: 2704
5. Feldman BJ, Murray RW (1987) Inorg Chem 26: 1702

6. Hamnett A, Higgins S, Mortimer RJ, Rosseinsky DR (1988) *J Electroanal Chem* 255: 315
7. Dostal A, Meyer B, Scholz F, Schroder U, Bond AM, Marken F, Shaw SJ (1995) *J Phys Chem* 99: 2096
8. Kuhnhardt C (1994) *J Electroanal Chem* 369: 71
9. Kaneko M, Okada T (1988) *J Electroanal Chem* 255: 45
10. Neff VD (1985) *J Electrochem Soc* 132: 1382
11. Hartmann M, Grabner EW, Bergveld P (1991) *Anal Chim Acta* 242: 249
12. Kulesza PJ, Doblhofer K (1989) *J Electroanal Chem* 274: 95
13. Deakin MR, Byrd H (1989) *Anal Chem* 61: 290
14. Itaya K, Akahoshi H, Toshima S (1982) *J Electrochem Soc* 129: 1498
15. Ellis D, Eckhoff M, Neff VD (1981) *J Phys Chem* 85: 1225
16. Kelawi H, Rosseinsky DR (1982) *J Electroanal Chem* 131: 373
17. Carpenter MK, Conell RS (1990) *J Electrochem Soc* 137: 2464
18. Monk PMS, Mortimer RJ, Rosseinsky DR (1995) *Electrochromism, fundamentals and applications*, ch 6. VCH, Weinheim
19. Duek EAR, De Paoli MA, Mastragostino M (1992) *Adv Mater* 4: 287
20. Yano J, Kai S, Ogura K (1993) *J Mater Science Letters* 12: 1791
21. Mortimer RJ, Rosseinsky DR (1983) *J Electroanal Chem* 151: 133
22. Mortimer RJ, Rosseinsky DR (1984) *J Chem Soc Dalton Trans* 2059
23. Plichon V, Besbes S (1990) *J Electroanal Chem* 284: 141
24. Kulesza PJ (1990) *J Electroanal Chem* 289: 103
25. Kulesza PJ, Zamponi S, Berrettoni M, Marassi R, Malik MA (1995) *Electrochim Acta* 40: 681
26. Zamponi S, Czerwinski A, Marassi R (1989) *J Electroanal Chem* 266: 37
27. Zhang C, Park SM (1988) *Anal Chem* 60: 1639
28. Zamponi S, Czerwinski A, Gambini G, Marassi R (1992) *J Electroanal Chem* 332: 63
29. Itaya K, Ataka T, Toshima S (1982) *J Am Chem Soc* 104: 3751
30. Siperko LM, Kuwana T (1983) *J Electrochem Soc* 130: 396
31. Robinson RA, Stokes RH (1959) *Electrolytic solutions*, 2nd edn. Butterworths, London, pp 120–126
32. Lundgren CA, Murray RW (1988) *Inorg Chem* 27: 933
33. Feldman BJ, Melroy OR (1987) *J Electroanal Chem* 234: 213
34. Bacskai J, Martinusz K, Czirok E, Inzelt G, Kulesza PJ, Malik MA (1995) *J Electroanal Chem* 385: 241
35. Cotton FA, Wilkinson G (1980) *Advanced Inorganic Chemistry*, 4th edn. Wiley, pp 762–763
36. Sinha S, Humphrey BD, Bocarsly AB (1984) *Inorg Chem* 23: 203