JOURNAL OF APPLIED ELECTROCHEMISTRY **22** (1992) 325–331

Electrochemical studies of the factors influencing the cycle stability of Prussian Blue films*

D. E. STILWELL†, K. H. PARK‡, M. H. MILES

Chemistry Division, Research Department, Naval Weapons Center, China Lake, CA 93555, USA

Received 30 April 1991

Some of the factors leading to long term cycle stability for Prussian Blue (PB) films are determined. The pH of the conversion electrolyte was found to be the overwhelming factor in film stability; cycle lifetimes in excess of 100 000 were easily achieved in solutions of pH 2–3. Concurrent with the increase in stability at lower pH was a considerable increase in switching kinetics. Surprisingly, the films grown from chloride-containing solutions were found to be slightly more stable, in terms of cycle life, compared to those grown from chloride-free solutions. In addition, we found that there occurs at least some conversion of PB form during the first cycle, and thus, form conversion kinetics cannot be evoked as a mechanism for film stability. Unfortunately, the films grown electrochemically on ITO glass exhibited a white haze which we attribute to light scattering caused by grain size. Unless it can be eliminated, this haze effect will be a serious drawback in the eventual use of PB in an electrochromic filter. Finally, the films were stable in mixed solvents that provide an expanded temperature range, and preconditioned films were stable to drying and immersion in boiling water

1. Introduction

Our interest in Prussian Blue (PB) centres on the possible use of this material to work in a complementary fashion with WO_3 or viologen materials in an electrochromic based optical filter. Prussian Blue is a well known compound with an extensive history, both in coordination chemistry and in the dying industry, over the past 250 years. Nonetheless, the first report on the electrochemistry of PB modified electrodes is relatively recent [1]. Following this initial report by Neff, extensive studies have been carried out on the electrochemistry of PB [2–27] and on related transition metal hexacyanide compounds [28–33]. A recent review on the electrochemistry of PB is available [34]. Apart from the electrochromic applications for PB, other uses that have been proposed include, solid-state batteries [14–18], sensors [2], separations [19], photochargeable devices [20–23], as well as for electrocatalytic applications [24–27] such as the reduction of CO_2 to methanol [24, 25].

In general, PB may be described as a mixed valent compound belonging to the class $M_K^A[M^B(CN)_6]$, where M^A and M^B denote transition metals. The electrochromic response of the PB system is produced by the electrochemical oxidation of the colourless Prussian White (PW)

$$\underbrace{K_2FeFe(CN)_6}_{PW} \rightleftharpoons K^+ + \underbrace{KFeFe(CN)_6}_{PB} + e^- \qquad (1)$$

to form the blue coloration. Comprehensive reviews on the chemistry of mixed valent compounds have been written [35–38]. There are two forms of PB, the so-called 'soluble' ($KFeFe(CN)_6$) and the 'insoluble' ($Fe_4[Fe(CN)_6]_3$). These terms originate not from any differences in solubility, but rather in the ease of peptization [8, 34, 35, 39]. The peptization of PB results in the formation of a colloidal dispersion. Mortimer and Rosseinsky [8] have stressed the unsuitability of these terms (soluble and insoluble). Ellis *et al.* [39] have pointed out that both forms are highly insoluble ($K_{sp} = 10^{-40}$). Nevertheless, this nomenclature has been carried forward in the literature, and will be used here as well.

Despite the impressive advances that have been achieved in these studies, very little work has been published on the quantitative aspects affecting film stability. The identification and understanding of the underlying mechanisms behind these stability factors (such as cycle life, shelf life, and dissolution kinetics) are very important considerations for any practical application of PB based devices.

In a survey of the PB literature we could only find three values which have been reported for cycle lifetime. Itaya's group has reported cycle lifetimes of up to 5×10^6 cycles for films switched between the PB and the reduced (PW) states in 1 M KCl. The pH was adjusted to 4 with HCl and the films were not dried after deposition. Conversely, Kellawi and Rosseinsky [12] could only obtain a cycle lifetime of 20 using the solution composition described above. They did

---

* Portions of this paper were originally presented at the Fall meeting of the Electrochemical Society, held in Hollywood FA (1989).

† Present address: Connecticut Agricultural Experiment Station, New Haven, CT 06504 USA

‡ Present address: Argonne-West, Idaho Falls, ID 83403, USA

report that stability enhancement (3600 cycle lifetime) was achieved in saturated $KClO_4$ solutions with pH adjusted to 4 using H_2SO_4. In their study, however, a more positive oxidation potential limit was employed such that the Prussian Blue film was also converted to the higher oxidized form (Berlin Green). Finally, Dong and coworkers [13] could find no difference in the voltammograms for PB films subjected to as many as 200 cycles in 1 M KCl.

Some researchers have addressed the stability issue qualitatively. The results of an ellipsometric investigation [3] has shown that PB films become thinner after each conversion cycle in $KClO_4$ (0.1 M) solution. There are references indicating that a post deposition drying sequence increases stability [4, 5], while others suggest that the film should always remain wet [2, 3, 7, 9–11]. Feldman and Murray [7] have provided photomicrographic evidence that cracking can occur in the PB film upon drying. Obviously, film cracking is detrimental to film adhesion and would scatter the light in an electrochromic device. Studies on PB films have been carried out in salt solutions, either with no pH adjustments [2–5, 13], or with the pH adjusted to some acidic value, usually 4 [6, 7, 9–12]. It has been pointed out that $Fe(OH)_3$ could be produced in solutions above pH 6.4 [6]. Mortimer and Rosseinsky [40] mentioned that a pH 2 in the deposition solution was optimal for stabilization of a subsequent film form of ferric ferricyanide (Prussian Brown).

The PB film deposition conditions that have been reported vary considerably. The typical parameters for film growth include galvanostatic, potentiostatic, pH, ferricyanide concentration, supporting electrolyte, as well as composition and concentration of the iron (III) salt [2–27].

There is very little literature that provides any solid evidence for favouring one particular growth method over another. One study [3], based on ellipsometry, concluded that more uniform films result in agitated solutions employing low current density [$4\,\mu A\,cm^{-2}$). Others argue that potentiostatic control can result in a more homogeneous film, and that the constant applied potential insures that all of the film is initially in the mixed valent state [4]. The use and composition of the supporting electrolyte has been shown to have little effect on the film form [8]. For example, the so-called insoluble form of PB (containing no K^+) was always obtained using KNO_3 supporting electrolyte concentrations ranging from zero to 3.6 M.

Most workers use $FeCl_3$ as the ferric ion source, although other salts such as $Fe_2(SO_4)_3$ have been employed [12]. The rationale behind the prevalent use of $FeCl_3$ is unclear since this material is difficult to prepare in the pure form. Most importantly, if the ideal PB structure is to be obtained then it must be assumed that the chloride ligands are removed. Ligand removal is a necessary prerequisite for forming the neutral $FeFe(CN)_6$ adduct. It is believed that PB films are the reduction product of this adduct [34, 41]. The assumption of complete chloride ligand removal is probably not valid. Film analysis has shown that considerable amounts of chloride (Fe : Cl = 9 : 1) remain in the films after deposition from solutions containing the ferric chloride precursor [4]. Moreover, this chloride is tenaciously bound; it is not exchanged by other anions in solution, nor is it removed during the first few reduction cycles. These findings have led to the suggestion that the chloride is, in fact, strongly coordinated and not an interstitial species [4].

2. Experimental details

The electrochemical measurements were carried out with a PAR model 173 potentiostat/galvanostat with the model 179 digital coulometer and the model 175 universal programmer accessories. For the electrochemical cell, we employed a standard three-electrode system contained in a dual compartment cell. A fine porosity frit was used to separate the working and counter electrodes. Either a Ag/AgCl (saturated KCl) or a saturated calomel electrode (SCE) was used for the reference electrode. The current-voltage data was either acquired on an *x–y* recorder, or by using a computer data acquisition system (Analog Device RTI-815).

The working electrodes were either platinum basket type electrodes (area = $14\,cm^2$), or ITO conducting glass (Optical Coating Laboratory, Inc. (OCLI) Santa Rosa, CA, area $1–5\,cm^2$, sheet resistance = $5\,\Omega\,cm^{-2}$, 90% transmission). The platinum electrodes were pre-cleaned in concentrated HNO_3 while the ITO electrodes were pre-cleaned in 1 M NaOH solution. The electrodes were rinsed well with distilled H_2O, and were stored in H_2O prior to use. The electrodes were removed from the water and, while still covered by the water layer, placed into the deposition solution. The deposition conditions and post treatments varied and are discussed in the following section.

The PB film thickness was estimated from the cathodic charge consumed in the first reduction cycle (PB to PW, +0.6 to −0.2 V/SCE). A film density of $1.6\,g\,cm^{-3}$ was used to compute the film thickness. This value for the density is the average between the reported values of $1.4\,g\,cm^{-3}$ [9], and $1.78\,g\,cm^{-3}$ [42]. In cases where the absorption spectrum was obtained (on ITO glass), the thickness was also calculated from the absorbance. These values agreed to within 20% with the thickness derived from the charge method. In calculating the thickness from absorbance measurements, a molar absorptivity of $9800\,L\,mol^{-1}\,cm^{-1}$ was used for the soluble form. For the insoluble form, the values used were $7300\,L\,mol^{-1}\,cm^{-1}$ (with respect to Fe^{3+}), and $9800\,L\,mol^{-1}\,cm^{-1}$ (with respect to Fe^{2+}) [9, 10, 43–46]. In other words, for the insoluble form ($Fe_4[Fe(CN)_6]_3$), the concentration of PB is $1.86\,mol\,L^{-1}$ (based on density), thus, the Fe^{3+} and Fe^{2+} concentrations in the PB films would be 7.44 and $5.58\,mol\,L^{-1}$, respectively. The insoluble form was taken to exist in the fresh film, and conversion to the purely soluble form was assumed after one reduction/oxidation cycle. Based on the above, the calculated film thickness ranged from 0.04 to $0.3\,\mu m$ depending on deposition time (1–5 min).

A typical cycle life test was performed as follows. First, the film was preconditioned in the test electrolyte by potential cycling for one-half hour between +0.6 to −0.2 V/SCE with a scan rate of 50 mV s^{-1} [2]. The potential was then held at +0.6 V for 3 min to establish equilibrium prior to acquiring a voltammogram (same potential range and sweep rate as above). The cathodic charge was measured and the film was then subjected to x number of potential cycles (square wave +0.6 to −0.2 V at 1 Hz). After x cycles, the potential was held for 3 min and the voltammogram was taken, as described above. We define the stability factor as the ratio of the voltammetric cathodic charge after x potential pulses divided by the charge measured for the first cycle after preconditioning.

The chemicals were all reagent grade, and used as received. Anaerobic conditions were maintained with a nitrogen or argon atmosphere.

3. Results and discussion

3.1. *Growth methods*

First, we tried to establish a correlation between growth methods and film stability. In the first part of the growth study, representative PB film deposition procedures found in the literature were employed [4, 5, 9, 10]. The resulting films were then tested for stability by continuously cycling in 1 M KCl between the potential limits of +0.6 to −0.2 V with a scan rate of 50 mV s^{-1} in most studies. Post-deposition treatments included drying in air, in a desiccator, or in a vacuum oven (20–110° C, 1 h to 3 days), or not drying at all, and dipping in $FeSO_4$ [5]. In the next phase of the growth study, we developed a deposition solution composition based on a sulphate buffer (with and without any chlorides). The sulphate buffer solution composition was 0.2 M K_2SO_4/0.05 M H_2SO_4 (calculated pH 2.2 based on pK_{a2} 1.98 [47, 48], 0.02 M $K_3Fe(CN)_6$, and either 0.02 M $FeCl_3$ or 0.02 M $Fe(ClO_4)_3$. We found that solutions could be readily prepared with ferric perchlorate which contained no suspended particles, whereas those made with ferric chloride tended to readily form colloidal precipitates [1]. The absorbance of both of these solutions peaked at 419–420 nm which confirms the formation of the $FeFe(CN)_6$ adduct [34, 35, 41]. In terms of suspended particles, higher quality solutions resulted if the $Fe(ClO_4)_3$ was dissolved prior to adding the rest of the salts. After adding the remainder of the salts, the mixture was warmed on a hot plate to dissolve the sulphates. The advantages of using a sulphate buffer include a well defined pH, no H^+ concentration gradient, and that the high supporting electrolyte concentration minimizes the ion migration currents. Moreover, when ferric perchlorate is used, there can be no possibility of chloride contamination in the freshly deposited film, coordinated [4], or otherwise entrained. The films prepared using the sulphate buffer solution were all deposited potentiostatically at +0.5.V/SCE for 1–5 min in unstirred solutions.

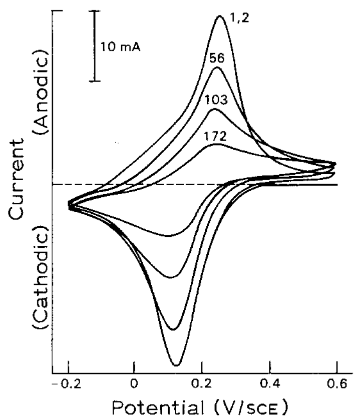

Fig. 1. Typical results for cycle stability of PB films on the Pt substrate in 1 M KCl. This film was continuously cycled at a scan rate of 50 mV s^{-1}; the numbers on the figure represent the cycle number. This film was grown galvanostatically according to the procedures outlined in [5], and then dried in a vacuum oven at 105° C for 3 h (films dried overnight in air exhibited even poorer cycle stability). The calculated initial film thickness was 0.1 μm.

Typical voltammograms taken in 1 M KCl are shown in Fig. 1. Although the films that were dried or heat treated exhibited more stability, none of the films showed a cycle life of more than 100–300 (a cycle lifetime is defined as the number of cycles to reach one-half of the charge measured at some starting point). Even though the drying procedures tended to increase cycle life somewhat, in many cases, and particularly when heated in the vacuum oven, this increase was at the expense of inferior electrochromic responses (i.e., portions of the film remained blue, regardless of potential). We attribute this loss of response to a dehydration which renders the film resistance so high that an insulating barrier is formed. Alternatively, the PB film may have lost physical contact with the substrate; however, no signs of any gross peeling of flaking were noted.

3.2. *pH effects*

After failing to establish any long term film cycling stability in neutral KCl solutions, we focused on determining cycle stability in acidic solution. For this portion of the study, the films were all deposited potentiostatically at +0.51 V/SCE from the sulphate buffer solution described above. The films were rinsed with water but not dried prior to immersion in the solution used for the cycle life tests (the test, or conversion electrolyte).

The remarkable stabilization effect in solutions at pH 2 are shown in Figs 2 and 3. Note in Fig. 2 that the peak height increases somewhat with cycle number. This increase in peak height, however, is accompanied by a decrease in peak width; the net result being a slight decrease in the measured charge. Finally, after about 10^5 potential pulses in KCl/HCl at pH 2, the voltammograms (and thus the film) tend to stabilize, as shown in Fig. 3. The decrease in peak width may be due to either a loss of, or a slow conversion of, the iron species characterized by the shoulder oxidation peak centered at around 0.05 V. This shoulder peak has

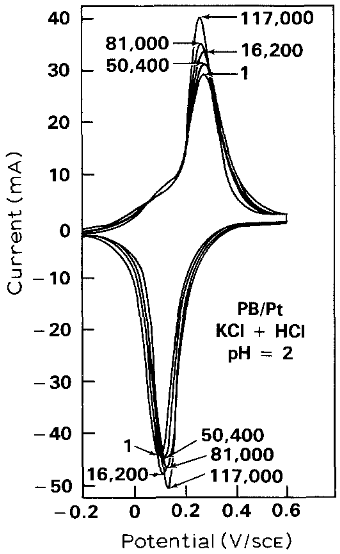

Fig. 2. Typical results showing the stabilization of pH on PB films grown on a Pt substrate. The numbers on the figure are the number of 1 Hz cycles that the PB film was subjected to prior to taking that voltammogram. The electrolyte was 0.9 M KCl in 0.010 M HCl aqueous solution. See text for other experimental details (scan rate = 50 mV s^{-1}).

been discussed in detail by Murray's group [4, 7]. They assigned the electroactive ferric state with the less positive potential (the shoulder peak) to a hexa-coordinated iron with isocyano ligands (-NC). The electroactive iron species associated with the larger more positive peak was attributed to unsymmetrically coordinated iron with -NC, water, and possibly -Cl ligands. These assignments are consistent with our observations during the long term cycling studies, as some ligand exchange of the isocyano group with water or chloride is certainly plausible.

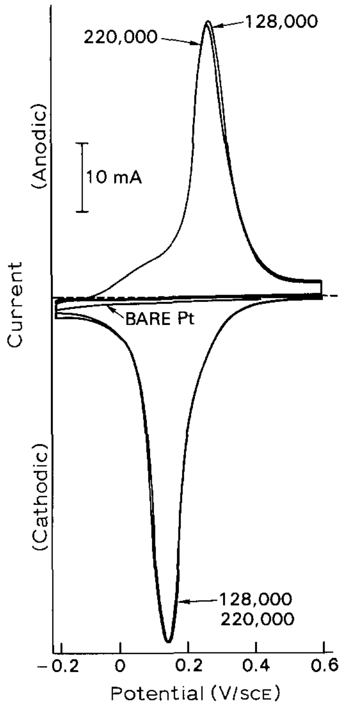

Fig. 3. Same film and conditions as shown in Fig. 2.

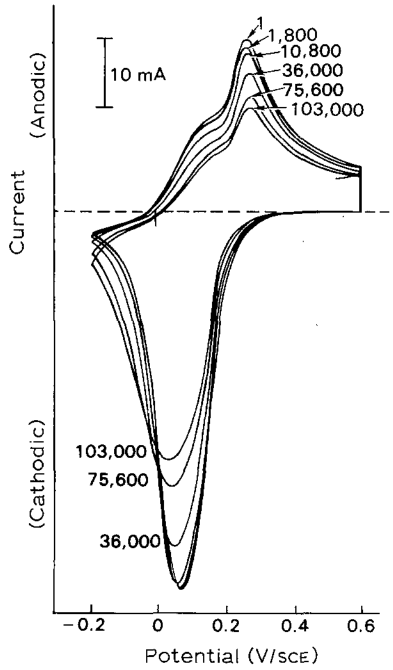

Fig. 4. Voltammograms of a PB film on Pt substrate in an aqueous 0.125 M H_2SO_4, 0.5 M K_2SO_4 solution (pH 2.2). The calculated initial film thickness was 0.23 μm. See Fig. 2 and text for other conditions (scan rate = 50 mV s^{-1}).

Cycle stability tests were also carried out in sulphate buffer electrolytes (pH 2.2), and a typical result is shown in Fig. 4. There are a number of significant differences in the behaviour in this buffer compared to the unbuffered electrolyte. The most striking difference is that the oxidation shoulder peak is considerably enlarged and can be almost fully resolved in terms of peak potential. This feature contrasts the reduction behaviour where the two reactions are apparently merged to give a broad reduction peak. Furthermore, the film is decidingly less stable, and the voltammograms decrease monotonously with the cycle number. This steady decrease suggests an etching mechanism whereby a portion of the film is slowly converted to an authentic soluble form. This conversion may be due to a transition of the hexacoordinated ferric species into some unsymmetrically coordinated form which dissolves into the electrolyte. Finally, note that at potentials positive to the last oxidation wave, the current does not fall to near baseline values. This effect could be due to the introduction of a large capacitive component to the current, similar to what is observed in conducting polymers [49, 50]. The fact that the peak remains relatively sharp seems to rule out any drastic change in the charge transfer kinetics.

The stability factors for the PB films against cycle number are shown in Fig. 5. All of the films shown here were deposited from the sulphate buffer using $Fe(ClO_4)_3$, except for the film denoted as (a) where the ferric source was $FeCl_3$. As typified by the behaviour of film (a), PB films deposited from chloride solutions are as stable, and perhaps, even slightly more stable than those prepared in the same fashion but without chlorides. This finding suggests that the coordinated chloride could act as an inhibitor in the dissolution process. The difference in stability reflected by films (d) and (e) are probably due to

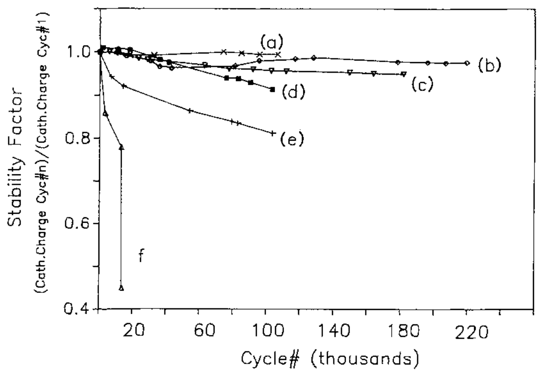

Fig. 5. Cycle stability for PB films on Pt under a variety of conditions: in, (a) 0.9 M KCl, 0.020 M HCl; (b) same electrolyte as (a); (c) 0.9 M KCl, 0.0010 M HCl; (d) and (e) 0.125 M H_2SO_4, 0.5 M K_2SO_4; (f) 1 M KCl. The calculated initial PB film thickness was 0.1, 0.16, 0.1, 0.23, 0.16, and 0.16 μm for entries (a)–(f), respectively.

the variation between films rather than a thickness effect.

The films tended to be considerably less stable when deposited on ITO glass, as shown by Figs 6 and 7. The reasons for this effect are unclear, but it may be related to substrate composition (ITO against Pt or SnO_2) or substrate pretreatment. The method of SnO_2 manufacturing as well as the pretreatments of the substrate can be critical factors in the resulting quality of the PB film [44]. The large peak separation is likely due to the conducting glass electrode resistance [5, 9, 51, 52].

Finally, it should be pointed out that an increase in the switching speed was observed in the acidic electrolytes. The switching speed increased from about 2 s at pH 7 to about 0.2 at pH 2, as reflected by the sharper peaks (compare Fig. 1 to Figs 2 and 3). This interesting observation has considerable application as a fast switching speed is desirable for displays, filters and optical storage devices. Further work is needed to quantify this observation.

3.3. *Mixed solvent effects and post treatments of pre-conditioned films*

For military applications that require an expanded temperature range −40 to 110° C), water alone cannot be used as the electrolyte solvent in acceptable electrochromic devices, hence the behavior of PB in mixed solvents was investigated.

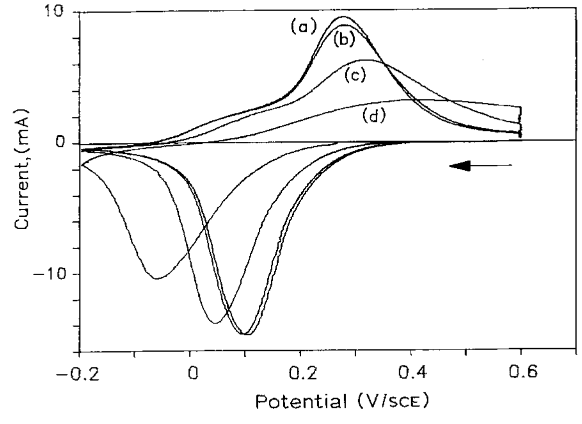

Fig. 6. Cycle stability of PB on ITO substrate. Voltammograms at 50 mV s^{-1} taken after (a) 1, (b) 3 600, (c) 18 600, and (d) 41 700 1 Hz cycles, in 0.9 M KCl, 0.010 M HCl aqueous solution. ITO area = 2.4 cm^2. The calculated initial film thickness was 0.3 μm.

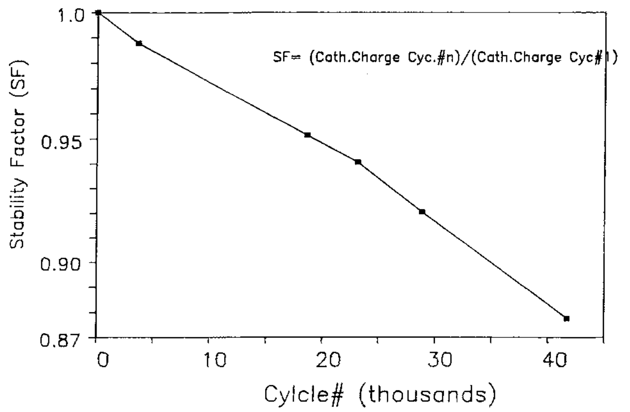

Fig. 7. Stability factor versus cycle number for the film shown in Fig. 6.

The cycle stability of a PB film on Pt in an acidified H_2O-ethylene glycol (EG) solvent mixture (35 wt % EG) is shown in Fig. 8. The H_2O–EG mixture was prepared by adding ethylene glycol to the 0.9 M KCl, 0.02 M HCl solution. Prior to immersion in the mixed solvent, the film was cycled for one-half hour (as described earlier), and then cycled 10 000 times (1 Hz) to establish that this particular film was stable. The sharper peaks at the slower scan rates has been observed previously [4].

In the mixed solvent, the peak width broadens a bit at the expense of a somewhat lower peak height, and

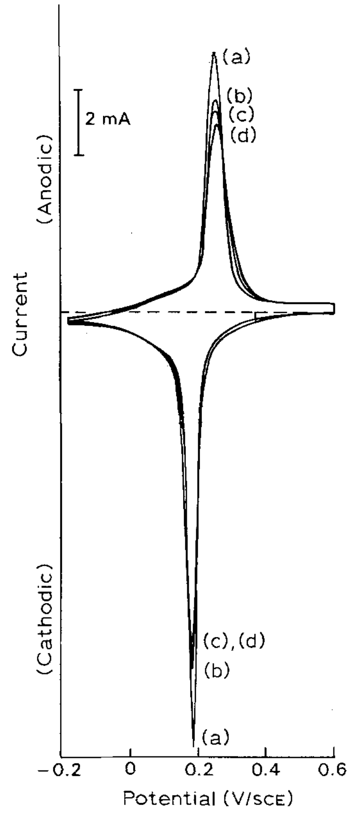

Fig. 8. Mixed solvent effects on the PB film using the Pt electrode. (a) In the aqueous KCl/HCl pH 2 solution; (b) first cycle in the water/EG mixture; (c) after 15 000 cycles; (d) after 48 000 cycles. Scan rate = 5 mV s^{-1}. See text for additional details.

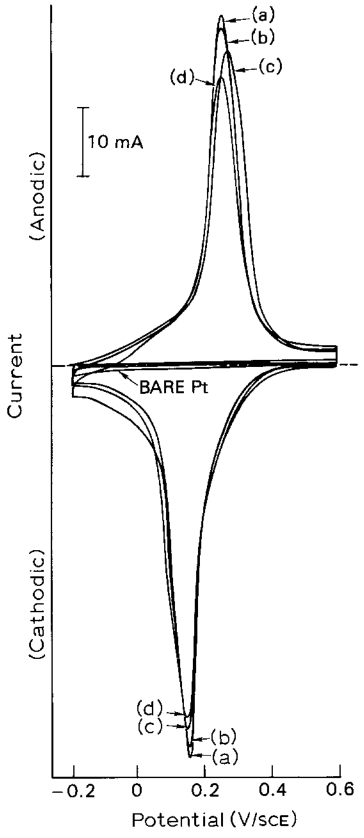

Fig. 9. Post-treatment effects on a pre-conditioned PB film. (a) After 220 000 cycles (see Fig. 3), and after drying in vacuum for 2 h at 60° C; (b) after (a) and after 12 000 cycles; (c) after 29 000 cycles; (d) after (c) and after immersion in boiling water for 10 min. Scan rate = 50 mV s^{-1}.

thus, the total charge remained relatively constant. The cathodic charge for voltammograms b–d in Fig. 8 were 152.2, 151.1, and 156.6 mC, respectively, compared to an initial value of 164 mC in the KCl/HCl pH 2 electrolyte (Fig. 8a). The cycle stability, along with the retention of switching kinetics in mixed solvents, demonstrates that an expanded temperature range for the actual use of PB in a device is feasible.

In contrast to our observations on the detrimental effects of drying a freshly prepared PB film, we found very little effects when a pre-conditioned film was dried. Shown in Fig. 9 are voltammograms of a PB film, that after being subjected to 220 000 cycles (Fig. 3), was then dried in vacuum, cycled 30 000 times, followed by immersion in boiling water. It seems that a pre-conditioned film is considerably more robust to post-treatments than the fresh film. This finding has important processing considerations since it is much easier to fabricate and assemble a dry device.

3.4. *Spectral properties*

The absorbance spectra for PB taken during the first reduction sequence of a freshly prepared PB film on ITO glass is shown in Fig. 10. Note that the absorbance peak red-shifts as the potential is decreased. The shift indicates the mixed nature of the reduction process, as well as the nonapplicability of Beer's law [44] for the PB to PW transition.

It was noted visually that films on the ITO remained somewhat milky, or hazy in the bleached state (PW). This haze problem is illustrated by the nonzero intercept at −0.2 V. The formation of this haze has been ascribed to a mismatch of refractive indexes between SnO_2 and PW [44]. We believe, however, that this haze could be caused by light scattering due to grain size of the PB microcrystalline particles, similar to the effects of grain size on AgCl based photochromic glasses [53]. It has been shown that it is possible to minimize this haze by changing the substrate [44]. Other possible ways of dealing with this problem are the changing of the electrochemical deposition conditions, or the use of an electroless deposition method that produces amorphous films [54].

The peak absorbance shifted from 725 to 689 nm at 0.6 V after just one cycle; a feature that has been observed in other studies [4, 8]. Mortimer and Rosseinsky [8] have suggested that this change in peak wavelength is diagnostic for form conversion of PB from the insoluble to the soluble form represented

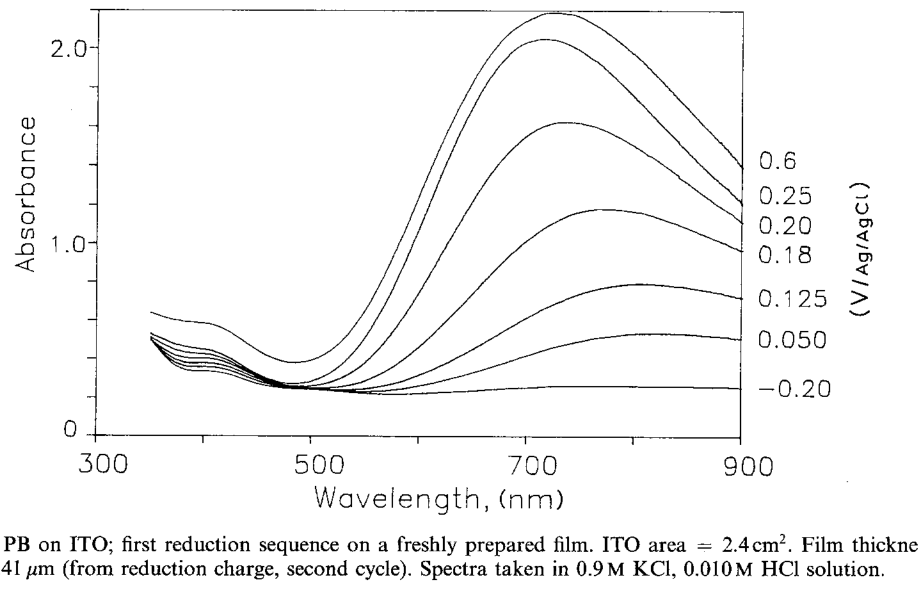

Fig. 10. Spectra of PB on ITO; first reduction sequence on a freshly prepared film. ITO area = 2.4 cm^2. Film thickness 0.38 μm (from spectra at 0.6 V); 0.41 μm (from reduction charge, second cycle). Spectra taken in 0.9 M KCl, 0.010 M HCl solution.

by

$$Fe_4[Fe(CN)_6]_3 + 3K^+ \longrightarrow 3KFeFe(CN)_6 + Fe^{3+} \quad (2)$$

If the postulate is true, and since some conversion has been shown to be rapid (one cycle), then the stabilization with acid cannot be due to a lowering of the kinetics of conversion from the insoluble to the soluble form. The pH effect would then be more likely due to a slower rate of conversion of -Fe–CN–Fe, or the Fe–CN–Fe–OH groups into soluble products. Further studies are needed to define the degradation mechanism.

4. Conclusions

The pH of the test solution was determined to be the most important factor determining cycle-life. Cycle lifetimes in excess of 100 000 with a contrast ratio of approximately 100 were readily achieved in KCl/HCl solutions of pH 2–3. Moreover, the switching speed was considerably faster in the acid solution. However, acid solutions containing buffers yielded lower cycle lifetimes when compared to the strong acid, suggesting that a base catalyzed intermediate step may be involved in the dissolution mechanism. The cycle stability in a mixed solvent was demonstrated, hence, an expanded temperature range for a PB device is possible. Finally, haze, most noticeable in the reduced form of the film, could be a serious problem for optical filter applications. This effect is probably related to grain size and film thickness. Further work needs to be done in order to establish the factors which could influence this haze.

Acknowledgment

This work was supported by Independent Research (IR) and Independent Exploratory Development (IED) funding provided by the Naval Weapons Center. Two authors (D.E.S. and K.H.P.) express appreciation for postdoctoral fellowships provided by the Office of Naval Technology and the American Society for Engineering Education (ONT/ASEE).

Portions of this paper were originally presented at the Fall 1989 meeting of The Electrochemical Society, Inc., held in Hollywood, Florida.

References

[1] V. D. Neff, *J. Electrochem. Soc.* **125** (1978) 868.
[2] M. R. Deakin and H. Byrd, *Anal. Chem.* **61** (1989) 290.
[3] D. J. Beckstead, D. J. DeSmet and J. L. Ord, *J. Electrochem. Soc.* **136** (1989) 1927.
[4] C. A. Lundgren and R. W. Murray, *Inorg. Chem.* **27** (1988) 933.
[5] J. W. McCarger and V. D. Neff, *J. Phys. Chem.* **92** (1988) 3598.
[6] B. J. Feldman and R. W. Murray, *J. Electroanal. Chem.* **234** (1987) 213.
[7] B. J. Feldman and R. W. Murray, *Inorg. Chem.* **26** (1987) 1702.
[8] R. J. Mortimer and D. R. Rosseinsky, *J. Chem. Soc. Dalton Trans.* (1984) 2059.
[9] K. Itaya, H. Akahoshi and S. Toshima, *J. Electrochem. Soc.* **129** (1982) 1498.
[10] K. Itaya, T. Ataka and S. Toshima, *J. Amer. Chem. Soc.* **104** (1982) 4767.
[11] K. Itaya, K. Shibayama, H. Akahoshi and S. Toshima, *J. Appl. Phys.* **53** (1982) 804.
[12] H. Kellawi and D. R. Rosseinsky, *J. Electroanal. Chem.* **131** (1982) 373.
[13] Li Fengbin and Dong Shaojun (F. Li and S. Dong outside of China), *Sci Sinica (Ser. B)* **30** (1987) 368.
[14] M. Kaneko and T. Okada, *J. Electroanal. Chem.* **255** (1988) 45.
[15] E. W. Grabner and S. Kalwellis-Mohn, *J. Appl. Electrochem.* **17** (1987) 653.
[16] M. Kaneko, *J. Polymer Sci: Part C: Polym. Lett.* **24** (1986) 435.
[17] K. Honda and H. Hayashi, *J. Electrochem. Soc.* **134** (1987) 1330.
[18] V. D. Neff, *ibid.* **132** (1985) 1382.
[19] T. Ikeshoji, *ibid.* **133** (1986) 2108.
[20] M. Kaneko, K. Takahashi and E. Tsuchida, *J. Electroanal. Chem.* **227** (1987) 255.
[21] A. Viehbeck and D. W. Deberry, *J. Electrochem. Soc.* **132** (1985) 1369.
[22] M. Kaneko, S. Hara and A. Yameda, *J. Electroanal. Chem.* **194** (1985) 165.
[23] K. Ataya, I. Uchida, S. Toshima and R. M. DeLaRue, *J. Electrochem. Soc.* **131** (1984) 2086.
[24] K. Ogura and I. Yoshida, *Electrochim. Acta* **32** (1987) 1191.
[25] K. Ogura and K. Takamagari, *J. Chem. Soc. Dalton Trans.* (1986) 1519.
[26] K. Itaya, N. Shoji and I. Uchida, *J. Amer. Chem. Soc.* **106** (1984) 3423.
[27] F. Li and S. Dong, *Electrochim. Acta* **32** (1987) 1511.
[28] K. Itaya, T. Ataka and S. Toshima, *J. Amer. Chem. Soc.* **104** (1982) 3751.
[29] J. A. Cox and B. K. Das, *J. Electroanal. Chem.* **233** (1988) 87.
[30] Dong Shaojun (S. Dong) and Fengbin Li (F. Li), *J. Electroanal. Chem.* **217** (1987) 49.
[31] S. J. Lasky and D. A. Buttry, *J. Amer. Chem. Soc.* **110** (1988) 6258.
[32] P. J. Kulesza and M. Faszynska, *J. Electroanal. Chem.* **252** (1988) 461.
[33] S. Dong and Z. Jin, *ibid.* **256** (1988) 193.
[34] K. Itaya, I. Uchida and V. D. Neff, *Acc. Chem. Res.* **19** (1986) 162.
[35] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.* **10** (1967) 247.
[36] B. M. Chadwick and A. G. Sharpe, *ibid.* **8** (1966) 83.
[37] A. G. Sharpe, 'The Chemistry of Cyano Complexes of the Transition Metals', Academic Press, NY (1976) Chapter 7, pp. 99–147.
[38] D. B. Brown (ed.), 'Mixed Valence Compounds', Reidel, Dordrecht (NATO Advanced Institute Series, Vol. 58) (1980) pp. 1–507.
[39] D. Ellis, M. Eckhoff and V. D. Neff, *J. Phys. Chem.* **85** (1981) 1225.
[40] R. J. Mortimer and D. R. Rosseinsky, *J. Electroanal. Chem.* **151** (1983) 133.
[41] J. A. Ibers and N. Davidson, *J. Amer. Chem. Soc.* **73** (1951) 476.
[42] A. Ludi and H. V. Gudel, *Struct. Bonding (Berlin)* **14** (1973) 1.
[43] M. B. Robin, *Inorg. Chem.* **1** (1962) 337.
[44] K. Itaya and I. Uchida,*Inorg. Chem.* **25** (1986) 389.
[45] P. S. Braterman, *J. Chem. Soc. A* (1966) 1471.
[46] G. Cheng and S. Dong, *Electrochim. Acta* **32** (1987) 1561.
[47] D. E. Stilwell and S.-M. Park, *J. Electrochem. Soc.* **136** (1989) 688.
[48] M. A. Paul and F. A. Long, *Chem. Rev.* **57** (1957) 1.
[49] D. E. Stilwell and S.-M. Park, *J. Electrochem. Soc.* **136** (1989) 427.
[50] S. W. Feldberg, *J. Amer. Chem. Soc.* **106** (1984) 4671.
[51] C.-H. Pyun and S.-M. Park, *Anal. Chem.* **58** (1986) 251.
[52] A. Desbene-Monvernay, P. C. Lacaze and A. Cherigui, *J. Electroanal. Chem.* **260** (1989) 75.
[53] R. J. Araujo, Photochromic Glasses, in 'Encyclopedia of Physical Sciences and Technology', Vol. 10, Academic Press, London (1987) pp. 425–33.
[54] T. Ozeki, I. Watanabe and S. Ikeda, *J. Electroanal. Chem.* **236** (1987) 209.