Short Communication

Cyclic voltammetric studies of Prussian blue and viologens within a paper matrix for electrochromic printing applications

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Abstract

The apparent redox response of Prussian blue (PB, iron(III) hexacyanoferrate(II)) within a paper matrix is similar to that found in conventional liquid electrolyte voltammetry using a PB-modified electrode; however part of the response is from PB which adsorbs onto the glassy carbon (GC) working electrode. Application of a Nafion® coating to the PB-impregnated paper matrix prevents transfer of PB to the GC surface. In contrast to the PB system, the redox response of the 1,1'-dimethyl-4,4'-bipyridilium (MV, methyl viologen) system, where both redox states examined are soluble, is confined wholly to the paper matrix. For the case of 1,1'-diheptyl-4,4'-bipyridilium (HV, heptyl viologen), the electrogenerated insoluble radical cation salt adsorbs onto the GC electrode, the KCl-impregnated paper acting simply as the electrolyte medium. PB can be electrogenerated within a paper matrix, with the possible application in monochrome electrochromic printing systems. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Chemical species that can be redox switched between different visible region electronic absorption bands are said to be electrochromic [1]. Printing systems based on this phenomenon have been proposed [2,3]. In operation, digitised images could be formed by directing voltage pulses to pixel electrodes, in contact with paper incorporating an electrochromic species and electrolyte, the non-image side of which rests intimately on a conducting surface comprising the counter electrode. An understanding of the electrochemical response of electrochromic species within a paper matrix is essential to the future development of electrochromic printing systems.

The apparent electrochemical response in paper of Prussian blue (PB, iron(III) hexacyanoferrate(II)), 1,1'-dimethyl-4,4'-bipyridilium (MV, methyl viologen) and 1-phenylhydroxyethyl-1'-methylbipyridilium has earlier been demonstrated [2]; however, the effectiveness of the colour switching was not commented upon. Here we explore the redox response in paper of some model electrochromic systems (PB [4–7], MV [8] and 1,1'-diheptyl-4,4'-bipyridilium (HV, heptyl viologen) [8,9]), consider the feasibility of their use in electrochromic printing modes, and give some direction to possible future research.

2. Experimental

2.1. Instrumentation and procedures for cyclic voltammetry

Cyclic voltammograms (CVs) were recorded using an EG&G Princeton Applied Research (PAR) Model 173 potentiostat interfaced to a MacLab/2e and operated...
using EChem software (AD Instruments) with a Macintosh LC computer. For conventional CVs a three-compartment electrochemical cell was employed using nitrogen-purged solutions, with a glassy carbon (GC) (0.2 cm² surface area) or Pt wire (0.32 cm² surface area) working electrode and a platinum-mesh counter electrode. Electrode potentials were measured and are quoted with respect to a Radiometer sodium chloride saturated calomel electrode (SSCE) at 22 ± 2°C. No IR compensation was employed. CVs using a paper matrix (‘fast filtration’ no. 41 Whatman filter paper) were carried out in the open laboratory with the damp impregnated paper laid on a pre-cleaned copper sheet (15 × 10 cm²) acting as counter electrode. The tip of the GC working electrode and the sinter of the SSCE were allowed to rest, under their own weight, on top of the paper [2].

2.2. Prussian blue studies

PB-modified GC electrodes were prepared by electroreduction (to 1 × 10⁻³ C cm⁻²) following a potential step from +1.00 to +0.50 V in an aqueous solution containing 5 mM FeCl₃·6H₂O, 5 mM K₃Fe(CN)₆, 0.2 M KCl and 0.01 M HCl [6]. For paper CV experiments, following initial loading with supporting electrolyte (1 h in 3 M KCl, and draining to (just) dampness), the filter paper was immersed in the above electroactive species solution. After pressing between absorbent sheets to remove any excess solution, photo reduction (60 W tungsten lamp illumination for 5 min) was carried out. In the present study, illumination generated a pale green colour due to formation of Prussian green rather than the reported PB [2]. For coating with Nafion®, the PB-impregnated paper was immersed in a 0.5 wt.% 1100 EW Nafion® 117 solution prepared by dilution of a 5 wt.% commercial solution (Aldrich) with 2-propanol.

2.3. Viologen studies

Solution CVs were carried out using 0.005 M 1,1'-dimethyl-4,4'-bipyridilium dichloride or 1,1'-diheptyl-4,4'-bipyridilium dibromide in 0.2 M aqueous KCl. For paper CV experiments, the paper matrix was impregnated with viologen and supporting electrolyte by soaking (1 h) in 0.005 M 1,1'-dimethyl-4,4'-bipyridilium dichloride or 1,1'-diheptyl-4,4'-bipyridilium dibromide, as appropriate, in 3 M aqueous KCl.

3. Results and discussion

3.1. Prussian blue electrochromicity

Fig. 1 demonstrates that the two PB redox waves for a PB-modified GC electrode are qualitatively the same as observed in a paper matrix experiment. Inspection of Fig. 1 shows the effect of varying the immersion time in the electroactive species solution in the initial impregnation stage. Brief immersion (10 s) yields a lower ΔEₚ value, indicative of a surface-confined species, in contrast to a longer immersion time (10 min.). For the PB/GC case, scanning cathodically from +0.50 V reduces PB reversibly, to Prussian white (iron(II) hexacyanoferrate(II)). The positive scan from +0.50 V generates Prussian yellow (iron(III) hexacyanoferrate(III)) reversibly via the intermediate Prussian green state [6,7]. To examine whether such polyelectrochromicity is observed in the paper matrix the working electrode was removed from the paper surface at a sequence of potentials. Results were disappointing; after initial electroreduction to the solid PB at +0.50 V, the paper retained the intense blue colour of PB, regardless of potential. It seems likely, that once ‘fixed’ as PB, although the CVs (Fig. 1) showed the usual redox waves, not all the PB in the paper matrix under the GC electrode was being redox switched. Fig. 2 shows that following a paper matrix experiment, if the GC electrode was transferred to the supporting electrolyte a CV response due to surface-confined PB is

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Fig. 1. CVs at 50 mV s⁻¹, initiated from +0.50 V in the negative direction. PB | GC electrode in 0.2 M KCl (—); PB/paper after 10 s (...) and 10 min (---) prior immersion in the electroactive species solution.
revealed. This result shows that the apparent PB redox current assumed [2] to represent PB confined within the paper matrix is at least in part due to PB adsorbed onto the GC electrode. The higher $\Delta E_p$ values observed when the impregnated paper acts as the supporting electrolyte medium will be due to the increased IR drop in this matrix and the lower availability of K$^+$ cations, which are important in the reversibility of the PB redox response [6]. Applying a coating of the sulfonated perfluorinated polyether Nafion® to the PB-impregnated paper matrix was found to prevent transfer of PB to the GC surface.

3.2. Viologen electrochromicity

Fig. 3 contrasts CVs for the MV$^{2+}$/MV$^{+*}$ redox wave in solution and within a paper matrix. In the latter case, the wave is electrocatalytic in nature due to reaction of the MV$^{+*}$ radical cation monomer/dimer with ambient oxygen. For this reason, the red colour of the MV radical cation dimer in the impregnated paper matrix was observed only briefly (ca. 2 s) on removal of the GC electrode at $-0.90$ V. Following a paper matrix experiment, transfer of the GC electrode to the supporting electrolyte revealed only a background CV response. In this case, the redox response measured (Fig. 3 (…)) is due wholly to the soluble MV redox system retained within the paper matrix.

Fig. 4 shows that the redox waves for HV in solution and within a paper matrix are qualitatively the same. In this case however, the expected crimson colour of the radical cation salt at the negative potential limit was not observed on removal of the GC electrode. On reduction, the HV dication forms an insoluble radical-cation salt on electrode surfaces, which on the reverse scan is stripped anodically, giving the sharp voltammetric wave. The redox waves observed (Fig. 4 (…)) are therefore interpreted as being due to electron transfer processes at the electrode interface, with no diffusion of coloured species into the paper matrix. Following a paper matrix experiment, removal at 0.00 V and transfer to supporting electrolyte revealed only a background CV response for the GC electrode, showing that the HV dication was not adsorbed onto the GC surface.

3.3. Combined PB and methyl viologen electrochromicity

Following the demonstration of five-colour poylelectrochromicity using a PB/Nafion® (MV) bilayer configuration [10], it was of interest to establish whether the PB and MV redox responses could be combined within a paper matrix. For this study, the paper was first impregnated with MV, followed by PB. The electroactivity observed was found to be a summa-
Fig. 4. CVs at 50 mV s$^{-1}$, initiated from 0.00 V in the negative direction. Pt electrode (---) in 0.005 M 1,1-diheptyl-4,4%-bipyridilium dibromide, 0.2 M KCl; impregnated paper (...) after prior immersion in 0.005 M 1,1-diheptyl-4,4%-bipyridilium dibromide, 3 M KCl.

4. Conclusions

The successful electrogeneration of PB within a paper matrix suggests that this material would be suitable for the investigation of electrochromic printing systems. However, only monochrome printing is feasible as once formed it is not possible to switch PB to the other coloured redox states. In contrast, for the MV system, as both redox states are soluble it is possible to switch between the different states. For colour printing, mixtures of soluble redox indicators within a paper matrix need to be investigated. A combination of redox indicators with a sequence of redox potentials would permit choice of colour by addressing the paper matrix with specific applied potentials. Although useful for demonstration of the principle, viologens would not be suitable in this application due to the rapid reaction of the coloured radical cation state with oxygen.

References