

Five Color Electrochromicity Using Prussian Blue and Nafion/ Methyl Viologen Layered Films

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Prussian blue films that can be switched to green and colorless redox states were first reported by Neff (1). Subsequently, electrodeposition conditions were revealed for the additional observation of a golden yellow redox state (2,3). The results reported here demonstrate that such polychromicity can be further extended to include a purple color state. The method involves application of an outer layer of the perfluorinated polysulfonate cation exchange polymer Nafion to a Prussian blue film (4). The methyl viologen dication (colorless)/radical cation (purple) system is then incorporated by ion-exchange into the Nafion.

Studies where Prussian blue films form part of a bilayer system have previously been restricted to Prussian blue/cupric hexacyanoferrate layered films (5). Nafion has only been used in connection with Prussian blue as a solid polymer electrolyte for the fabrication of a solid state electrochromic display device and rechargeable battery (6-8).

EXPERIMENTAL

All chemicals were Analytical Reagent grade. The Nafion 1100 EW 5 wt. % stock solution was supplied by Aldrich. Working electrodes were tin-doped indium oxide conducting glass ($20 \Omega/\square$, $5 \times 5 \text{ mm}^2$). A platinum mesh counter electrode and SSCE reference electrode were used. Electrochemical measurements were conducted using P.A.R. (E.G. & G. Instrument Co.) instrumentation. All solutions were outgassed with nitrogen.

Prussian blue films were electrodeposited by potential step from +1.00 to +0.50 V using a solution of 5 mM FeCl_3 , 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 0.2 M KCl in 0.01 M HCl. Nafion layers were prepared by applying the appropriate volume

of diluted stock solution with a microsyringe and allowing the solvent to evaporate.

RESULTS AND DISCUSSION

Figure 1a shows sequential CVs for the incorporation of methyl viologen into a Nafion film on a conducting glass working electrode. The Nafion surface concentration indicated was respect to sulfonate groups and provided the optimum thickness ($1.5 \mu\text{m}$) for maximal current of incorporated methyl viologen. The potential was scanned over the first reduction wave corresponding to the reduction of the colorless dication to the purple radical cation. The response is comparable to that for methyl viologen incorporated into Nafion films on graphite electrodes (9). Figure 1b shows the response on transfer to pure supporting electrolyte.

Figure 2a shows sequential CVs for the incorporation of methyl viologen into a Nafion outer layer on a Prussian blue film. The thickness of Prussian blue ($0.06 \mu\text{m}$, estimated from the charge for electro-deposition) provided comparable current to that for the methyl viologen system. All five color states are visually uniform across the electrode surface at the potential ranges indicated. Figure 2b shows the response on transfer to pure supporting electrolyte. The potentials for the Prussian blue redox processes (2) in Figure 2 are unchanged in the presence of the Nafion outer layer. In contrast, although the methyl viologen dication reduction occurs at a comparable potential to that in Figure 1, the oxidation of methyl viologen radical cation occurs over a wide potential range. The purple radical cation color is not fully discharged until electron-transfer mediation occurs at the onset of the Prussian white oxidation wave. That such irreversibility is a feature of the Prussian blue/Nafion/methyl viologen combination was shown by the reversibility of CVs for the methyl viologen solution redox

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process at both a bare conducting glass electrode and one with a Prussian blue film.

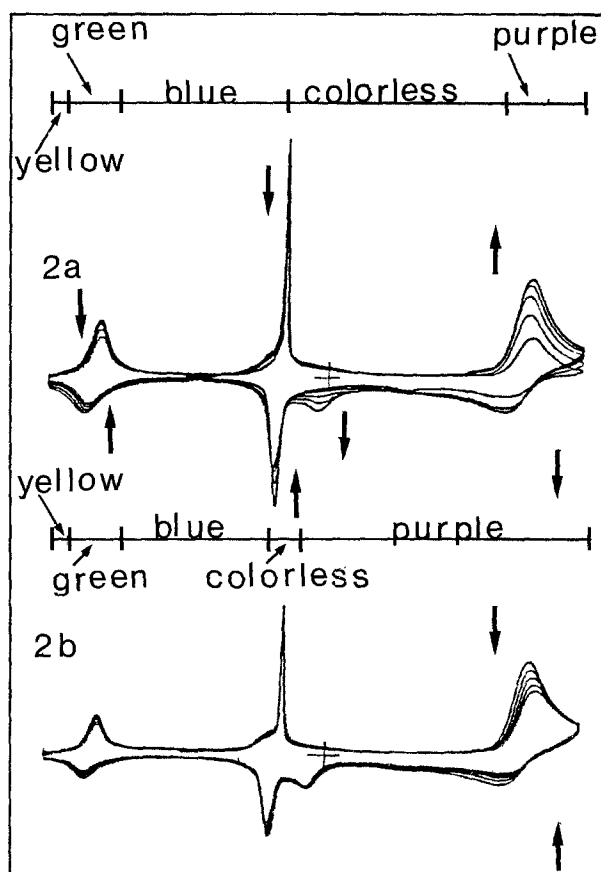
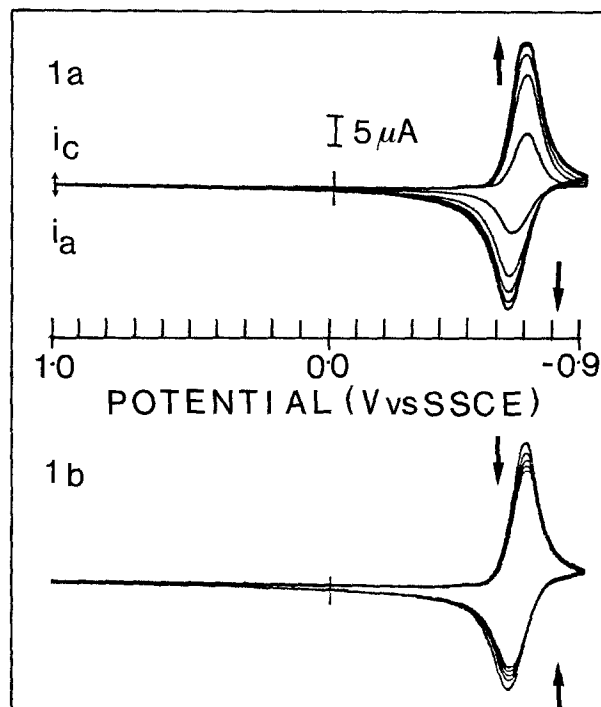
Studies are now planned to spectrally characterise the five color system, and to probe the irreversibility of the methyl viologen redox process shown in Figure 2. If the irreversibility could be optimised such that all the methyl viologen radical cation oxidation occurred by electron-transfer mediation then a system for unidirectional current flow would result. Such a system would be analogous to the bilayer redox polymer rectifying interfaces first demonstrated by Murray (10).

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Fig.1. CVs recorded at 10 mV s^{-1} directly after immersion of conducting glass electrode (with $2.14 \times 10^{-7} \text{ mol cm}^{-2}$ Nafion film) in solutions indicated. Potential scans initiated at +1.00 V and reversed at -0.90 V. The vertical arrows indicate current increase or decrease as appropriate. 1a. 0.1 mM methyl viologen and 0.2 M KCl. 1b. 0.2 M KCl after transfer from 1a.

Fig.2. CVs recorded at 10 mV s^{-1} directly after immersion of conducting glass electrode (with $1.2 \times 10^{-3} \text{ C cm}^{-2}$ Prussian blue film and $2.14 \times 10^{-7} \text{ mol cm}^{-2}$ Nafion outer layer) in solutions indicated. Potential and current scales as in Fig. 1. Potential scans initiated at +0.50 V, reversed at -0.90 V and +1.00 V. 2a. 0.1 mM methyl viologen and 0.2 M KCl. 2b. 0.2 M KCl after transfer from 2a.



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