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<http://dx.doi.org/10.1007/s10008-012-1811-7>

PUBLISHER

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VERSION

AM (Accepted Manuscript)

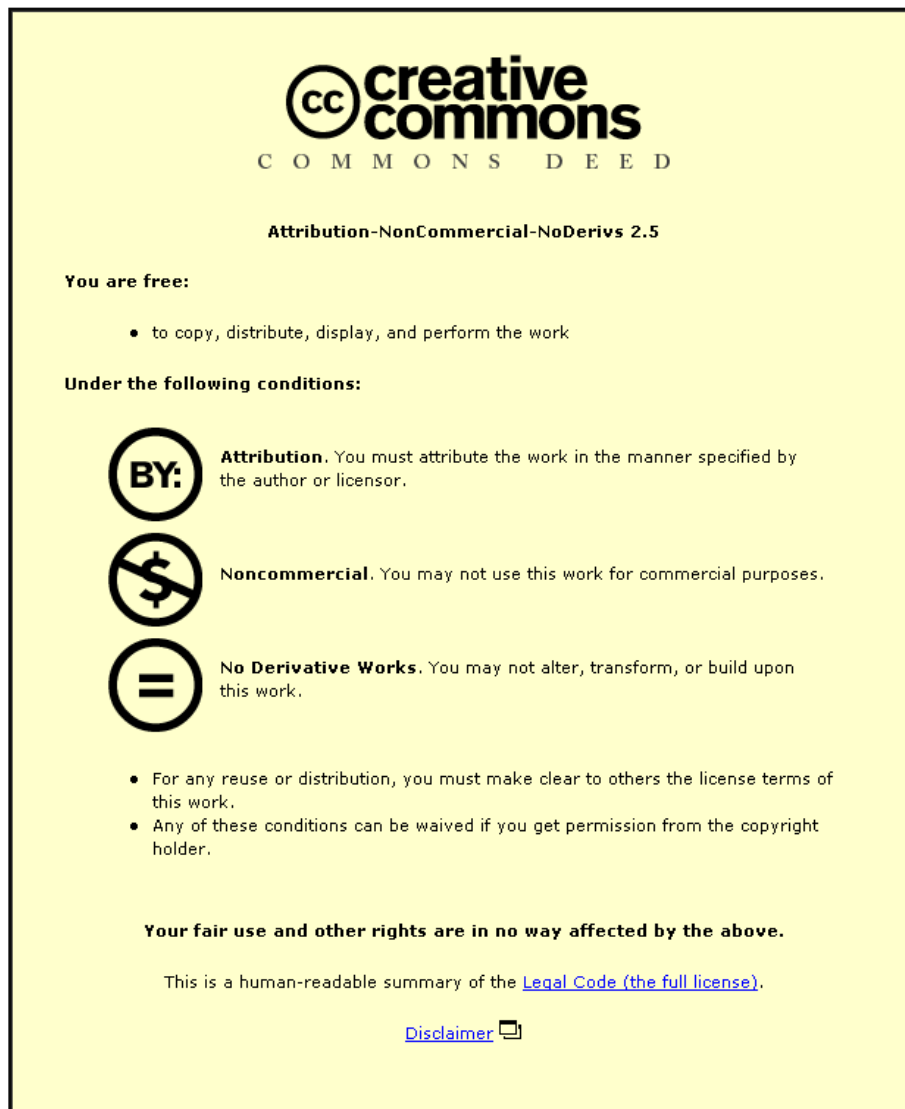
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Barton, Ray T., Hassan Kellawi, Frank Marken, Roger J. Mortimer, and David R. Rosseinsky. 2019. "Simplest Prussian-blue Deposition from Ferric Ferricyanide Solution by a Reducing Ag Spot Put onto an ITO Substrate". figshare. <https://hdl.handle.net/2134/11417>.

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Simplest Prussian-blue deposition from ferric ferricyanide solution by a reducing Ag spot put onto an ITO substrate

Ray T Barton • Hassan Kellawi • Frank Marken • Roger J Mortimer • David R Rosseinsky

Abstract Prussian blue (PB) film for electrochromism can be electro-deposited on to an electrode [usually tin-doped indium oxide /glass] either directly from a PB colloid, or from ferric ferricyanide in a two-electrode electrochemical cell by applying a reductive potential. Alternatively, a “sacrificial” electron-producing silver flag electrode in the solution, when connected to the PB-receiving electrode, can effect the required reductive deposition. A silver spot, here innovatively applied as silver paint *directly* onto the deposition electrode, produces PB film on immersion in the iron(III)(III) solution, obviating the separate counter-electrode method.

Key words: Prussian blue, thin films, silver, electrochromic

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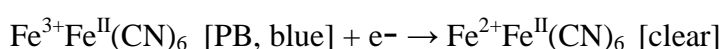
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Introduction

Prussian Blue (PB), “ferric ferrocyanide”, comprises a widely-used group of materials [1] $M^+Fe^{3+}Fe^{II}(CN)_6$ where M can be any alkali cation (or $\frac{1}{3}Fe^{3+}$ in the “insoluble PB” form). In historical and current use as a pigment [2], the colouration arises from the optical charge-transfer between the Fe^{II} and the Fe^{3+} . In recent decades Neff [3, 4] showed PB to be an electrochrome [1] of extensive applicability, as recently exemplified [5]. The PB electrochromic reaction, via externally-applied electrochemistry, is basically



where the reduced, clear, form is “Prussian White” (PW) [1]. The substrate is commonly transparent tin-doped indium oxide (ITO)/glass.

For PB electrochromism there are two main methods of preparation. Commonly, electro-deposition (electrochemical reduction) from ferric ferrocyanide solution, on to transparent conductive ITO/glass, is effected by an applied external potential [1] (note that Neff [3, 4] just immersed a pre-cathodised Pt or Au surface for the required reduction). Alternatively, colloidal PB has been directly electrodeposited straight onto the receiving electrode [6]. Ho [7, 8] introduced a variation of the former by using a separate silver metal electrode connected directly to the ITO also immersed in the iron(III)(III) deposition solution: sacrificial Ag dissolution causes reductive deposition of PB via the Ag-liberated electrons. Here, we describe the use of a silver metal spot directly applied to the ITO/glass, which, on total immersion of the assembly into the iron(III)(III) solution, undergoes just that sacrificial-silver reaction to produce a uniform PB film. This dispenses with the need of an electrochemical cell and a separate stand-alone Ag metal electrode. The Ag spot comprises silver paint as is commonly used to make external electrical connections to electrodes.

Experimental

Two sizes of ITO-coated glass (Image Optics Components Ltd., Basildon, Essex, typically $20\ \Omega$ per square), were used, either $0.9 \times 5.5\ \text{cm}^2$ (the lower $0.9 \times 4.0\ \text{cm}^2$ area is immersed in solution in electrochromic operation), or for larger electrodes, $20 \times 25\ \text{cm}^2$ (1.5 cm protruding atop in electrochromic use). The ITO/glass pre-cleaned in ethanol was sonicated in aqueous detergent for *ca* 1 h, well washed with tap water then de-ionised water (nominal $18.2\ \text{M}\Omega\ \text{cm}$). When dry a small spot of E1660-136 silver ink (a suspension of finely divided silver in a resin, from Ercon Inc., Wareham, MA, USA) was applied with a Pasteur pipette to give a thin spot of area $\sim 0.04\ \text{cm}^2$ onto a corner of the ITO/glass electrode. This Ag-spot ITO/glass was oven-dried for 1 h then cooled over silica gel.

The PB deposition bath comprised $0.002\ \text{mol dm}^{-3}\ \text{K}_3\text{Fe}(\text{CN})_6$ (BDH AnalaR) with HCl to pH ~ 3 -4, followed by slow addition with vigorous stirring of either solid $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (both Fisher Scientific for analysis) to $0.002\ \text{mol dm}^{-3}$; the pH avoided hydrolysis of the $\text{Fe}^{3+}(\text{aq})$. The resultant $\text{Fe}^{3+}\text{Fe}^{\text{III}}(\text{CN})_6$ complex is light brown in solution..

On immersion of the ITO/glass in the iron(III)(III) solution, the PB-forming reaction takes several minutes to deposit a uniform film on the smaller electrode. On the large electrode the deposition took several hours. Lighter PB deposits result by removing the Ag/ITO-glass/PB assembly from the deposition solution sooner. The PB films were well washed with DI water, drip-dried then kept in a desiccator over blue silica gel for reproducible H_2O content.

For electrochromism, the PB/ITO-glass electrode is immersed in an appropriate electrolyte-containing cell with a second, counter, electrode [1]. The preparative Ag spot is isolated here with say silicone cement if not employed as part of the external connection that is isolated from the echrome-cell electrolyte. This can be KCl solution [1] or an ionically conductive polymer [5].

Well-rehearsed in the literature e.g. [6], the widened CVs of thick PB (between ca -0.3 V and + 0.3 V vs the calomel electrode) are as previously recorded [1], while thin-film PB traces conform with the corresponding published CVs [9]. Ag-deposited PB is more uniform than ordinarily electrodeposited PB especially for large areas [7, 8], undergoing the on/off echrome reactions $PB + e^- \rightleftharpoons PW$ with satisfactory uniformity.

Discussion

A novel shortcut to PB electrodeposition, that employs just a single ITO substrate in the place of a preparative electrochemical cell, has been established here in a modified “sacrificial Ag anode” method, by using a silver spot deposited directly onto the PB-receiving electrode. The solution concentrations were not especially critical, as for example the ferric ferricyanide concentration when halved had no deleterious effect, only slowing the deposition. Faster deposition ensues with extra deposited Ag spots (alongside the original, to avoid subsequently insulated blots in the electrochromic area). Liberated Ag^+ will complex with deposition- solution species. The quality of deposited PB is entirely satisfactory (our trial Ag-flag deposited PB being initially less adherent, perhaps from poor deposition-cell geometry). In later experiments (McPhaden L, personal communication), ageing the original Fe(III)(III) solution in daylight for ≥ 48 h partly reduced the original solution to green, a well-known state [1], by photo-reaction with H_2O . The Ag-driven PB deposition was hereby markedly accelerated, a subject of ongoing research. The Ag spot method was foreseen in an early study [1, 10].

A just-published preparation [11] of a fine Ag network on glass, that is almost completely transparent and conductive (1Ω per square), promises highly uniform PB deposition by our method. Enough residual Ag might provide a conduction system free of ITO.

Acknowledgements

H K acknowledges leave from Damascus University.

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