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Electrochemical multilayer deposition of polyaniline and Prussian Blue and their application in solid state electrochromic windows

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In an attempt to enhance the solar modulation in electrochromic windows, the electrochemical deposition of polyaniline (PANI) and Prussian Blue (PB) has been studied more closely. Several layers of PANI and PB at different thicknesses have been electrodeposited on top of each other, or intermixed in the coating matrices. This intermixing, or multilayer deposition, of PANI and PB may lead to an overall improved coating performance. Integrating over the whole solar spectrum, a modulation as high as 49% of the total solar energy has been achieved in solid state electrochromic windows based on tungsten oxide (WO_3) and multilayer PANI–PB coatings, which is comparable to earlier results with a single PANI/PB layer.

Keywords: *electrochemical multilayer deposition*, *polyaniline*, *Prussian Blue*, *solid state electrochromic windows*, *cyclic voltammograms*, *transmission spectra*

1. Introduction

In earlier work [1, 2] we have fabricated electrochromic windows (ECWs) based on the electrochromic materials polyaniline (PANI), Prussian Blue (PB) and tungsten oxide (WO_3), which were electrochemically deposited on conducting indium–tin oxide (ITO) glass plates. The glass plates were glued together with the solid polymer electrolyte poly(2-acrylamido-2-methyl-propane-sulphonic acid) (PAMPS), the total glass sandwich being written Glass/ITO/PANI/PB/PAMPS/WO_3/ITO/Glass. PANI and PB coatings are complementary to WO_3, that is, PANI and PB attain a blue colour in the oxidized state (at positive potentials), while WO_3 has a blue colour in its reduced state (at negative potentials). Reversing the polarity, the coatings become bleached (transparent with no colour shades). Motivated originally by the work carried out by Leventis and Chung [3], PB was deposited on top of the PANI coating, as PANI has better adhesion properties to ITO than PB, whereas PB enhances the colouration significantly [1, 2]. Recent overviews of electrochromic materials may be found in Mortimer [4], Granqvist [5] and Monk *et al.* [6].

The object of this work is an attempt to improve the electrochemical deposition of PANI and PB, i.e. enhance the stability and solar light modulation of the ECWs. ITO glass plates were immersed in solutions consisting of PANI and PB forming chemicals at different concentrations. As PANI and PB are formed galvanostatically at positive and negative currents, respectively, the deposition current was switched back and forth between these levels at certain intervals (i.e., square current waves). Hence, layers of PANI and PB at different thicknesses were then deposited on top of each other, or intermixed in the coating matrices. In addition, depositions of PANI–PB multilayer films by changing electrolyte (PANI *or* PB forming chemicals) for each PANI or PB formation was also performed. Furthermore, potential cycling was employed in the electrodepositions, with the aim that this intermixing or multilayer deposition of PANI and PB might lead to an overall improved coating performance.

2. Experimental details

Several electrochemical deposition techniques, such as potential cycling, potentiostatic deposition, galvanostatic deposition and pulse deposition techniques, were employed in PANI–PB multilayer formation. Furthermore, different cell configurations and electrolyte compositions were applied, where in some experiments the PANI and PB forming chemicals were mixed together (both the working and counter electrode were ITO glass plates), while in other cases the ITO glass was immersed alternately in PANI and PB forming electrolytes. Note that PANI and PB are formed galvanostatically at *positive* and *negative* currents, respectively.

The PANI–PB coatings were deposited on ITO glass plates ($90\,\Omega\,\square^{-1}$), where only a few of these depositions will be further discussed here. The electrochemical PANI–PB deposition parameters for these film formations are given in Table 1, which summarizes the ECW configurations employed.

Table 1. Different electrochromic coating (PANI–PB, WO_3) deposition parameters for four selected electrochromic windows

Device	*PANI–PB deposition*	*WO_3 deposition*
A	Current square step $6.3\,\mu A\,cm^{-2} \rightarrow -6.3\,\mu A\,cm^{-2} \rightarrow 6.3\,\mu A\,cm^{-2}$ 90 s steps, total 9000 s Continuously stepping, i.e. no drying WE = ITO, CE = ITO	−700 mV for 300 s
B	PANI1: $15.6\,\mu A\,cm^{-2}$ for 2000 s, drying 1 h PB1: $-3.1\,\mu A\,cm^{-2}$ for 500 s, drying 1 h PANI2: $15.6\,\mu A\,cm^{-2}$ for 1000 s, drying 1 h PB2: $-3.1\,\mu A\,cm^{-2}$ for 1500 s	−700 mV for 500 s
C	PANI1: $29.9\,\mu A\,cm^{-2}$ for 2000 s, drying ½ year PB1: $-3.1\,\mu A\,cm^{-2}$ for 500 s, drying 1 h PANI2: $15.6\,\mu A\,cm^{-2}$ for 1000 s, drying 1 h PB2: $-3.1\,\mu A\,cm^{-2}$ for 1500 s	−700 mV for 300 s
D	PANI1: $15.2\,\mu A\,cm^{-2}$ for 2000 s, drying 3 days PB1: $-3.1\,\mu A\,cm^{-2}$ for 1500 s, drying ½ year PANI2: $15.6\,\mu A\,cm^{-2}$ for 1000 s, drying 1 h PB2: $-3.1\,\mu A\,cm^{-2}$ for 1500 s	−700 mV for 400 s

PAMPS was used as a solid state polymer electrolyte for the ECWs. For the PANI–PB deposition for device A the PANI and PB forming chemicals were mixed together (using two ITO glasses, both WE and CE), while for device B, C and D the ITO glass was immersed alternately in PANI and PB forming electrolytes. PANI1 denotes the first deposited PANI layer, PB1 the first deposited PB layer (on top of PANI1), and so on.

For ECW device A the electrolyte for the PANI–PB formation consisted of 0.01 M aniline, 0.25 M H_2SO_4, 0.25 M $KHSO_4$, 0.5 mM $K_3[Fe(CN)_6]$ and 0.5 mM $Fe_2(SO_4)_3$, using two ITO glass plates at the same time, that is, both the working electrode (WE) and counter electrode (CE) were ITO glass plates. (It should be noted that the mixture of acids and CN-compounds may start HCN evolution, and precautions must be taken.) For ECW devices B, C and D, the electrolyte consisted of 0.02 M aniline and 0.5 M H_2SO_4 for PANI formation and 0.5 M $KHSO_4$, 0.001 M $K_3[Fe(CN)_6]$ and 0.001 M $Fe_2(SO_4)_3$ for PB deposition (changing the electrolyte alternately between the different PANI and PB depositions). The different drying times for each layer of PANI and PB, before the next layer deposition, are indicated in Table 1.

The electrolyte for the WO_3 formation was prepared by dissolving 4.52 g of tungsten in 60 ml 30% hydrogen peroxide and diluting with distilled water to a total volume of 500 ml, thus giving a tungsten concentration of 0.049 M. All the WO_3 films were formed on ITO glass plates by applying a constant potential of −700 mV vs Ag/AgCl (3.0 M KCl) for 300, 400 or 500 s (refer to Table 1 for ECW construction). Before further use, the WO_3 films were heated at 140 °C for 1 h.

Platinum was used as a counter electrode for the electrodepositions of PANI, PB and WO_3 layers, while Ag/AgCl (3.0 M KCl) was used as reference.

The solid polymer electrolyte poly(2-acrylamido-2-methyl-propane-sulphonic acid) (PAMPS) was used to glue together the electrochromic electrodes for all device configurations, following a procedure described earlier [7], and sealed with epoxy. The electrochromic window area was 1.0 cm × 3.1 cm = 3.1 cm^2 (except for device A, where the area was 1.0 cm × 3.0 cm = 3.0 cm^2). The PANI, PB and WO_3 films were each less than 1 μm thick, while the PAMPS layer was about 0.1 mm. A schematic drawing of the electrochromic window configuration is shown in Fig. 1, with electrode reactions as described elsewhere [2].

Applying a positive potential (relative to the WO_3 electrode) to the PANI or the PANI/PB electrode, PANI, PB and WO_3 turned blue, while the window was bleached (transparent with no colour shades) by reversing the polarity of the electrodes.

An AutoLab PGSTAT20 potentiostat/galvanostat was used in the electrochemical deposition of PANI, PB and WO_3 films. The transmission experiments were carried out with a Cary 5 UV–VIS–NIR spectrophotometer in the 290–3300 nm wavelength region. Before recording the transmission spectra a constant potential was applied for several minutes with a Gerhard Bank Elektronik Göttingen Potentiostat MP81 in order to stabilize the colour changing films. A cell voltage (−1800 mV or + 1200 mV) was also applied during the wavelength scan.

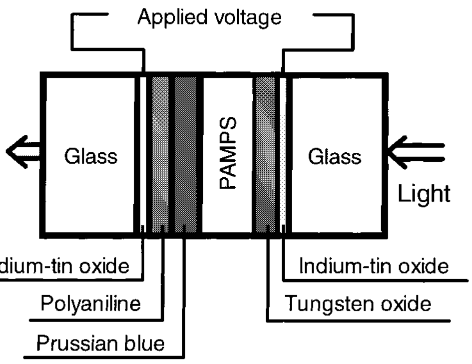

Fig. 1. Schematic drawing of the normal electrochromic window configuration based on the three electrochromic materials PANI, PB and WO_3.

3. Results and discussion

The results shown in the following includes PANI–PB multilayer film formations, cyclic voltammetry and transmission spectra for electrochromic windows.

Figure 2 depicts the current-voltage relationship during the PB film formation directly onto the ITO glass by potential cycling (0 mV → 1000 mV → 0 mV, 20 mV s^{-1}, 20 scans, electrolyte consisting of 0.5 M $KHSO_4$, 0.001 M $K_3[Fe(CN)_6]$ and 0.001 M $Fe_2(SO_4)_3$). The result was a rough PB film, parts of it falling off on removal from electrolyte. It should be noted that PB is formed at about 100 mV, while for potentiostatic PANI deposition the potential should be around 850 mV. Besides, PB is formed galvanostatically at *negative* currents while PANI is formed at *positive* currents. That is, the PANI–PB formation using a mixture of PANI and PB forming chemicals may be disrupted by the different deposition potentials and currents.

Generally, in the deposition of several layers of PANI and PB on the same electrode, there was a problem with the adhesion of the final PANI–PB film to the ITO glass. Upon removal from the formation electrolyte, large pieces of the film have often fallen off. However, the current stepping depicted in Fig. 3 yielded two beautiful blue coloured films. But unfortunately, a solid state ECW based on one of these films did not change colour (device A in Table 1, WE).

Four subsequent film formations are depicted in Fig. 4, that is, first one layer of PANI, thereafter one layer of PB, followed by one layer of PANI and finally one layer of PB. The result was a rough, very dark blue film, where the solid state ECW based on this film changed colour (device B in Table 1). The PANI–PB film formations for device C and D given in Table 1 yielded two rough, blue films, where both the solid state ECWs based on these films were able to change colour. To obtain sufficient film adhesion to the ITO glass, that is, to avoid parts of the film falling off, it was found necessary to dry the films in air for at least 1 h.

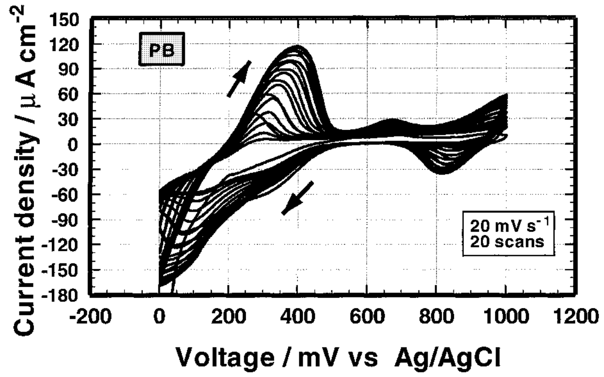

Fig. 2. Current density against voltage during formation of PB directly onto ITO by potential cycling. All peaks increase for about the first 10 scans, thereafter all decrease.

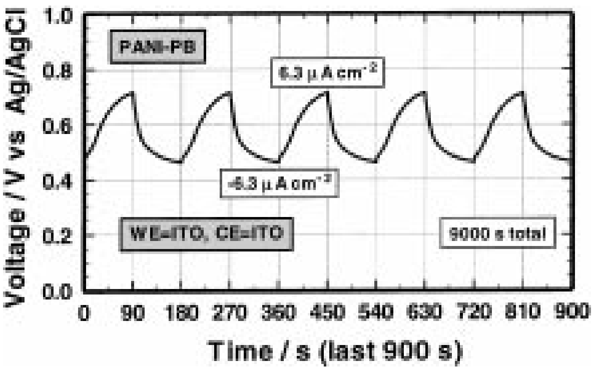

Fig. 3. Voltage against time during formation of PANI and PB applying square current waves, each step lasting 90 s. Corresponds to device A in Table 1.

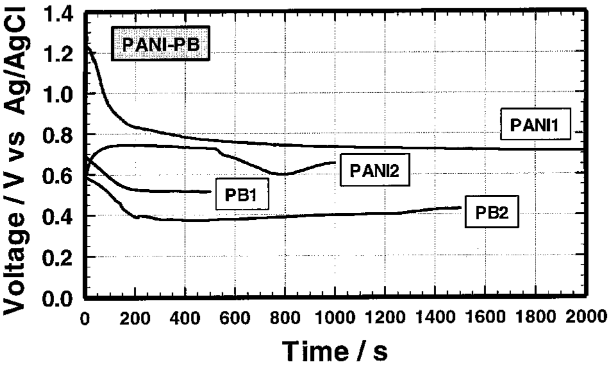

Fig. 4. Voltage against time during galvanostatic formation of PANI–PB multilayer film. The first layer of PANI was formed at 15.6 μA cm^{-2} for 2000 s, PB1 at −3.1 μA cm^{-2} for 500 s, PANI2 at 15.6 μA cm^{-2} for 1000 s and PB2 at −3.1 μA cm^{-2} for 1500 s. Each film was drying for 1 h before deposition of the next film. Corresponds to device B in Table 1.

Cyclic voltammograms between −1800 mV and + 1400 mV for the three colour changing ECWs B, C and D are shown in Figs 5–7. All three ECWs switched relatively slowly, i.e. the scan rate of 5 mV s^{-1} did not leave enough time to attain a clear transparent or dark blue colour. All the 10 voltammogram scans for each of devices B, C and D are almost identical (with only a minor deviation observed for the first scan), showing a generally good reversibility (Figs 5–7).

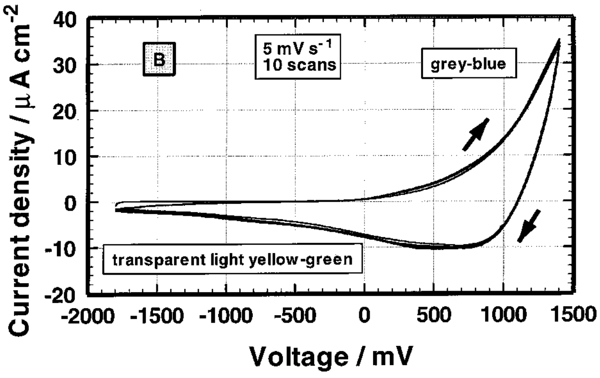

Fig. 5. Cyclic voltammograms for ECW device B. Ten cycles at a scan rate of 5 mV s^{-1}.

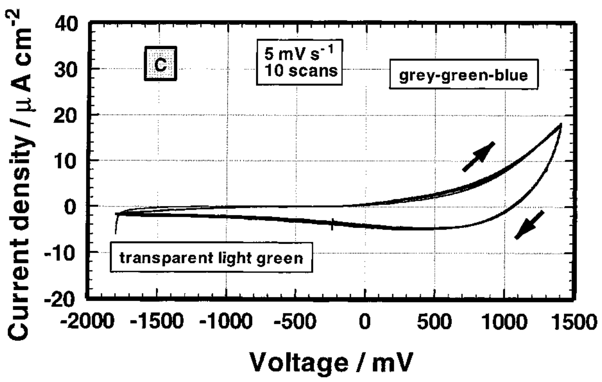

Fig. 6. Cyclic voltammograms for ECW device C. Ten cycles at a scan rate of $5\,\mathrm{mV\,s^{-1}}$.

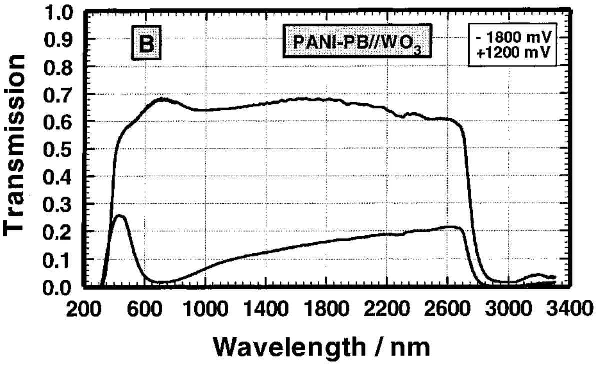

Fig. 8. Transmission against wavelength for ECW device B at −1800 mV and + 1200 mV.

It should be noted that devices B, C and D initially experienced a bleaching problem (the devices having a light green colour) associated with a characteristic absorption peak for PANI around 900 nm due to an obstruction of the necessary proton transfer in PANI as reported earlier [8, 9]. By stepping the potential between −1800 mV and + 1200 mV several times with potential hold periods from minutes to hours, the bleaching and colouring time decreased substantially, and the devices obtained a clear, transparent state or a dark blue colour, respectively, as may be seen in the transmission spectra (Figs 8–10). The origin of this wriggling effect, affecting positively the necessary proton transfer in PANI by stepping the potential back and forth, is still not clearly understood.

Transmission spectra in the 290–3300 nm wavelength region for the bleached (−1800 mV) and coloured (+ 1200 mV) state are given in Figs 8–10. It is observed that a large transmission modulation has been achieved for these three ECW devices, switching between a fairly clear, transparent state and a dark blue coloured state. Device B has an especially dark colour at + 1200 mV, for example, a transmission minimum as low as 1.4% between 700–720 nm, while at −1800 mV the transmission is 68% for the same wavelengths.

By taking into account the spectral distribution of the sunlight (i.e., the solar spectral irradiance [10]) and using the observed transmission spectra in Figs 8–10, the *solar transmission* for the ECWs in the bleached and coloured state can be calculated as shown earlier [1, 2]. Performing these calculations, it was found that devices B, C and D were each able to regulate as much as 49% of the total solar energy. This may be compared with our earlier reported results (49–50%) for electrochromic windows with PB deposited onto PANI [1, 2], that is, a significant higher modulation than 39% reported for ECWs based on PANI (and WO_3) without PB [2]. Furthermore, it should be noted that only preliminary experiments have been carried out, and optimization of film deposition parameters for PANI–PB may lead to improved coating performance.

4. Conclusions

Solid state electrochromic windows (ECWs) were made by incorporating PANI–PB multilayers. In preliminary experiments ECWs with a transmission modulation as high as 49% of the total solar energy were fabricated, which is comparable with earlier reported results (49–50%) for ECWs with PB deposited onto PANI. That is, a substantial higher modulation than 39% reported for ECWs based on PANI (and WO_3) without PB. It should be noted that the PANI–PB multilayer ECWs are

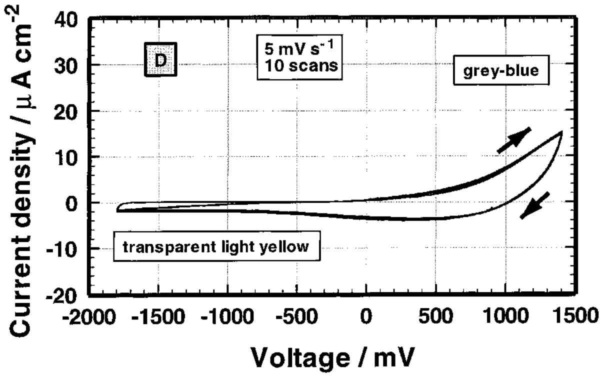

Fig. 7. Cyclic voltammograms for ECW device D. Ten cycles at a scan rate of $5\,\mathrm{mV\,s^{-1}}$.

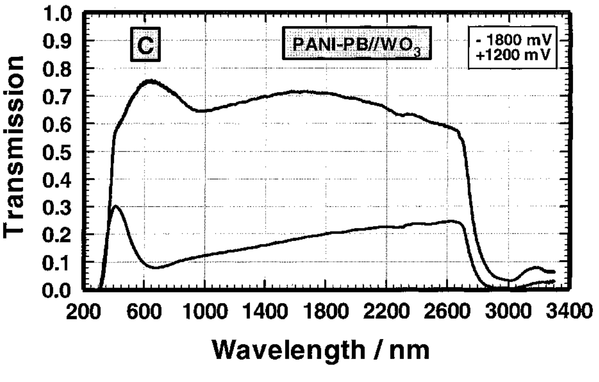

Fig. 9. Transmission against wavelength for ECW device C at −1800 mV and + 1200 mV.

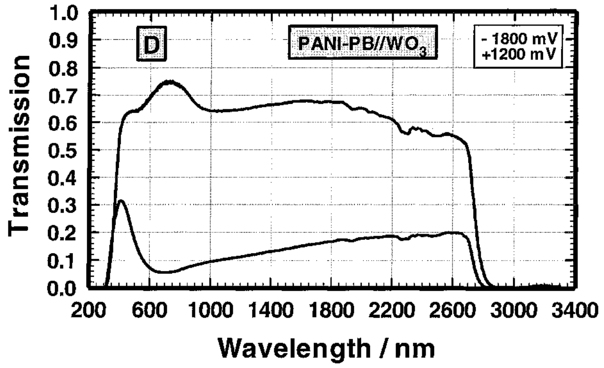

Fig. 10. Transmission against wavelength for ECW device D at −1800 mV and +1200 mV.

quite dark in the coloured state and, at the same time, able to regain a sufficient high transparency. However, the encouraging results obtained in these initial experiments indicate that further improvements in electrochromic performance of ECWs may be achieved by optimizing the multilayer deposition technique.

Deposition of PANI–PB multilayer films in electrolytes consisting of both PANI and PB forming chemicals have yielded some beautiful blue films, but which so far have not been able to change colour in solid state ECWs. On the other hand, depositions of PANI–PB multilayer films by changing electrolyte for each PANI or PB deposition have yielded films which change colour in solid state ECWs with a high solar modulation. The film drying time in air seems to be crucial for the following PANI–PB depositions, at least 1 hour should be considered a minimum.

Acknowledgements

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