

“Electrochromic Effects from a Simple Commercial Polymer Membrane”

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A simple commercial polyester polymer membrane has been found to exhibit an intense electrochromic effect. Most polymers which undergo electrochromic effects contain either transition metals or extensive conjugated systems. We have found that a simple commercial polyester membrane when coated with gold and polarised to -4 V (vs. Ag) in aprotic organic solvents displays an electrochromic colour change from a colourless to an intense red state.

Keywords. Polyester, electrochromic, cyclic voltammetry, ionic liquid, organic polymer.

1. Introduction

An electrochromic material is one where a reversible colour change takes place upon reduction (gain of electrons) or oxidation (loss of electrons), on passage of electrical current upon the application of an appropriate electrode polarising potential [1]. A large number of chemical moieties have been found to exhibit this effect. Recent reviews [2,3] describe many of these materials, however the polymers utilised are often complex materials which are not commercially available and may display limited stability to oxygen and water. Materials that display electrochromic effects include inorganic films such as tungsten oxide [2] and many transition metal complexes, whether in solution or incorporated within solid films [4-6]. Polymer films have also been formulated to display this effect, usually either by incorporation of redox-active species such as viologens within the film [7,8] or by use of conducting polymers such as polythiophene [9], polypyrrole [10,11] or polyaniline [12-14]. For example a recent publication [15] describes the formation of red, green and blue electrochromic polymers based on conducting polythiophenes which show a high stability and reversibility (10000 double potential cycles). Electrochromic polymers have a wide range of potential applications, including "smart windows", reusable labels and display devices [2,3].

We have recently discovered an entirely new class of high visibility electrochromic materials that change colour via an electronic effect that has previously not been recognised. A particular advantage of these electrochromic materials and the effects they exhibit is that they consume very little power during the colour change and consume virtually no power thereafter to maintain the colour. Whilst working on electrodepositing polymer layers onto simple commercial membranes, we have found

that polarising the membranes at cathodic potentials causes a colour change from a colourless state to an intense red colour. Our initial experiments involved depositing polydivinyl benzene membranes onto porous supports for utilisation within electrochemical glucose and lactate sensors [16-18]. It was noticed whilst electrodepositing these films onto polyester membranes, that the membranes changed colour [17, 18]. No colour change occurred when alumina membranes were used as supports [16]. We found that the presence of the monomer was not necessary to the process and that electrochromism still occurred in simple organic electrolyte solutions. Polyesters have been utilised previously in electrochromic devices, however they have not been the active constituent of the device but rather a flexible support for electrochromic layers of materials such as tungsten and niobium oxides [19]. This is, to our knowledge, the first time such a transition has been observed for a simple polyester membrane.

Commercial polyester membranes were evaporation-coated with gold on one side to make them electrically conducting. They were then placed into an organic solvent containing an organic electrolyte and polarised up to -4 V vs. a silver reference electrode. A variety of polymer membranes, solvents and metal coatings were utilised.

2. Experimental

All chemicals were obtained from Sigma-Aldrich. Acetonitrile and DMF were of HPLC grade. The electrochromic solutions were obtained by dissolving tetrabutyl ammonium perchlorate (0.2 M) in either DMF or acetonitrile. The choline/glycerol and choline/ethylene glycol ionic liquids were formulated as reported [6]. Electrolube® silver conductive paint (Electrolube® Ltd, Berkshire, UK) was

purchased from Maplins Electronics, Manchester, UK. Silver wire (0.5 mm diameter) and platinum gauze were purchased from Blundells (London, UK).

Cyclopore™ 0.2 µm polyester (polyethylene terephthalate) membranes, Cyclopore™ 0.4 µm polycarbonate membranes, 0.2 µm polyethersulphone membranes, 0.2 µm PTFE membranes, 0.2 µm nylon membranes, 0.45 µm polypropylene membranes, 0.2 µm polyamide membranes and Anopore™ 0.1 µm alumina membranes were purchased from Whatman International, Maidstone, UK. 0.4 mm polyester filter membranes were also purchased from GE Osmonics (MN, USA). Melinex polyester film (0.1 mm thick) was purchased from HiFi Industrial Films (Herts, UK).

The membranes were coated using an Edwards E480 evaporator. Films consisting of a single metal were 50 nm in thickness. In the case of gold-chromium films, 5 nm of chromium was evaporated, immediately followed by 50 nm gold. Multicore wires were attached to the coated membranes via the application of 'Electrolube®' silver conductive paint. The wire/electrode joint was then insulated with a coating of epoxy resin, which also served to enhance the mechanical strength of the electrode.

The electrochromic measurements were performed in a glass cell of volume 200ml (Figure 1). The metal-coated membrane was used as the working electrode, silver wire as the reference and platinum gauze for the counter electrode. The electrodes were positioned in a removable glass stage, which served to maintain a constant distance between the electrodes. The connections to the electrodes were able to enter the cell through three stoppered and sealed entry holes in the lid.

A Sycopel PCI 100 MK3 potentiostat computer interface was used in conjunction with a 'Ministat Potentiostat', (H.B. Thompson and Associates, Newcastle upon Tyne, UK) for all electrochemical measurements. The potential of the polymer electrode was cycled from 0 to 4 V (vs. Ag) and back at a rate of 50 mV s⁻¹. Colour co-ordinates of the resultant film were obtained using a CR-400 Chroma Meter (Konica Minolta). The visible spectrum of the polyester was measured in reflectance (the presence of the gold film prevents measurement of transmission spectra) utilising a DH-2000 light source combined with a USB2000 Miniature Fibre Optic Spectrometer (Ocean Optics, FL, USA).

3. Results and discussion

3.1 Electrochromism of polyester membranes.

The cyclic voltammogram of the system is shown in figure 2. As can be seen there is a clear transition occurring in the region of -2V. Repetitively sweeping the potential back and forth for up to 20 cycles did not affect the voltammogram.

Figure 3 shows the colour change that occurs as a potential is applied to the polyester membrane which is suspended in a 0.2 M solution of tetrabutyl ammonium perchlorate in DMF. As the potential reaches -2V vs. Ag, a colour change is observed to begin (stage 1). As the potential becomes more negative this colour change spreads over the surface (stage 2) and at -4V vs. Ag, the membrane assembly has become completely red (stage 3). The same effect could be obtained by simply applying a -4V polarisation to the membrane and led to complete colour change in <5 seconds. After being polarised at -4V for approximately 20s, current flow dropped to zero, indicating no further transitions take place. Setting the potential to 0V, removing the connection

(open circuit) or removing the polymer film from the solution caused rapid reversal (<5 seconds) to the original state. This process could be repeated for at least 20 cycles, however delamination of the gold film was found to eventually occur and at this stage the colour change ceased to occur.

Figure 4 shows the spectrum of the "red" polyester membrane. As can be seen there are two major adsorption peaks centred at approximately 420 and 580 nm. A unpolarised membrane was used as the background spectrum. Below 300 nm, the polyester in both cases adsorbed so highly that no spectrum could be obtained, i.e. all of the radiation was adsorbed. Measurement of the colour co-ordinates of the resultant red membrane (Fig 3, stage 3) gave $L = 39.1$, $C = 38.6$, $h = 14.2^\circ$ - which appears to the human eye as a claret/scarlet red.

3.2 Variation of the metal coating.

Due to the delamination of the gold film, other metals were investigated. Firstly, in an attempt to stabilise the gold film, a thin layer of chromium was evaporated onto the surface of the membrane and then gold was evaporated on top of this. This had no effect on the observed electrochromic effect, the intense red colouration still being observed. The gold film was however stabilised and this allows the electrochromic colour changes to be reversibly cycled for at least 200 cycles.

A thin film of silver could also be utilised and was found to give a strong colouration, identical to that observed with the gold and gold-chromium films, however repeated cycling did eventually cause delamination of the metal coating from the membrane surface. Chromium films were also utilised, however, in this instance the

electrochromic effect was only transient and the metal films were found to discolour rapidly, possibly indicating a corrosion effect. Aluminium coatings were found to give similar results to chromium.

3.3 Variation of solvent.

Acetonitrile, which has a good ability to solvate organic electrolytes, was utilised in place of DMF. When gold-chromium coated polyester membrane were polarised as before, colour changes identical to those in DMF were observed. As a possible substitute for an organic solvent/organic electrolyte mix, two ionic liquids [20] based on choline chloride combined with either ethylene glycol or glycerol were investigated instead, although in this case no electrochromic effect was observed. This could be due to low conductivity of the liquid as a result of its high viscosity.

3.4 Variation of membrane

Polyester membranes from GE Osmonics were also gold coated and tested and showed identical electrochromic effects to the Whatman membranes. However when a non-porous, thicker sheet of Melinex polyester was utilised, no electrochromic effect could be observed. This indicates that there must be good penetration of the solvent and electrolyte into the membrane for the electrochromic effect to occur. Probably the highly resistive nature of the Melinex sheet inhibits any electrochromism. This may explain why the electrochromic effect has not previously been observed for polyester since although polyester substrates have been utilised as supports in many previous electrochromism studies, they have been materials of the Melinex type rather than porous membranes.

As an alternative to the polyester membrane, other materials were used. These included glass microscope slides, alumina membranes and membranes based on polyamide, polypropylene, polycarbonate, polyethersulphone, polytetrafluoroethylene and nylon. These were all coated with gold and polarised at potentials between 0 and -7V vs. Ag wire. In all cases, no electrochromic effect could be observed.

3.5 Variation of electrolyte

Several electrolytes were tested as alternatives to tetrabutyl ammonium chlorate. Replacement of the chlorate with the corresponding tetrabutyl ammonium bromide had no effect, with a strong red colour still being generated. No electrochromism was observed when 0.2 m lithium chloride or perchlorate (in DMF) or sodium iodide (in acetonitrile and DMF) were used. It is thought that at the high potentials used the electrolyte is reacting rather than the polymer membrane. This is confirmed in the case of NaI by the rapid appearance of a yellow/brown colour in the solution attributed to iodine formation.

3.6 Mechanism of the transition.

We have described within this paper a strong electrochromic effect that occurs as a polyester membrane is polarised at strongly negative potentials. There are several possible explanations for this behaviour, although some of these can be ruled out. At first we thought that perhaps the solvent was being decomposed electrochemically to form a coloured product; however the use of two different solvents, DMF and acetonitrile allowed an identical electrochromic effect to be seen. A colouration of the metal film can also be ruled out since both gold (with and without chromium) and silver gave similar results. The electrochromic effect was however only observed

when polyester membranes were used, with other membranes of similar physical form - but composed of different polymers, giving no effect. We therefore conclude that the polymer itself must be taking an active part in this phenomenon.

The cathodic potential at which the electrochromic transition occurs indicates that electrons are being injected into the polymer structure. Polyethylene terephthalate has the structure shown in figure 5a with the conjugated terephthalate unit being the most likely moiety to which electrons can be added. We propose a mechanism where either one or two electrons can be added to the terephthalate unit to give either a radical (figure 5b) or diradical (figure 5c) structure as shown. What is interesting is that a resonance structure exists (figure 5d) where the unpaired electrons combine to give a non-radical dianion which could stabilise the structure.

4. Conclusions

We have reported here a novel electrochromic system which gives a strong red colour based on a simple commercial polymer membrane. Although the current system is unlikely to be commercially viable, the fact that such simple materials undergo a strong colour change indicates the possibility of a range of new materials.

Future investigations will involve chemical modification of the membranes to see whether other colours can be attained. Also the potential required for the electrochromic effect is relatively high compared to many others in the literature [2,3], modification may reduce this voltage. Finally attempts will be made to replace the organic electrolyte with a less volatile and toxic alternative such as a suitable ionic liquid or a solid electrolyte.

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Legends to Figures.

Figure 1: Experimental set-up for electrochromism studies.

Figure 2: Cyclic voltammogram of a gold coated polyester membrane from 0 to -4V (vs. Ag wire) in 0.2 M tetrabutyl ammonium perchlorate/DMF.

Figure 3: Reversible electrochromic colour change from a colourless to a deep red state.

Figure 4. Adsorption spectrum of the red polyester film, measured in reflectance mode.

Figure 5: Structure of (a) polyethylene terephthalate, (b) a possible radical anion, (c) a possible diradical dianion, (d) resonance structure of the dianion.

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