

SHORT COMMUNICATION

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Electrochromic window based on polyaniline

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Abstract A portable electrochromic display window (7 cm × 5 cm) has been constructed using a polyaniline-coated SnO₂ glass plate and an AlCl_{3(aq)} melt. The window colour can be switched from dark green to yellow or colourless by applying a small voltage of -0.5 to 2.5 V. It exhibits a fast response time (ms) and a long cycle life (1000).

Key words Electrochromism · Conducting polymer

Introduction

Although conducting polymers have been shown to have the potentialities for several applications, only a few of these have been demonstrated [1–3]. One important application of conducting polymers is electrochromism. Polyaniline is best suited for this purpose. Polyaniline shows different colours depending on the oxidation state. It has been investigated for the mechanistic pathways and suitability for several practical applications. We report here a practical demonstration of the electrochromism of polyaniline using an AlCl_{3(aq)} melt containing ppm levels of Ag ions. The response time and cycle life of a portable window developed using this electrolyte are also reported.

Experimental

Large display plates of SnO₂ glass (7 cm × 5 cm) were cleaned with trichloroethylene and washed well with acetone and distilled water

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before use. For recording the cyclic voltammetry, a Ag/AgCl or SCE was used. Platinum mesh (2 cm × 2 cm) was used as the counter electrode. The working electrode was constructed with either Platinum or SnO₂ glass plate. A PAR 273 potentiostat/galvanostat was used for all the experiments described here. The instrument was interfaced with an IBM-compatible computer for data acquisition and analysis.

Chemicals

Aniline (S.D. Fine Chemicals) was purified by distillation, and the fraction (colourless) boiling at 180 °C was used for the formation of the polymer. AlCl₃ and HClO₄ (S.D. Fine Chemicals) were used without any purification. *p*-Toluenesulfonic acid (Koch-Light), H₂SO₄ (BDH, LR grade), and trichloroethylene (S.D. Fine Chemicals) were used as received.

Polyaniline deposition

Polyaniline was deposited by either potential-step electrolysis or constant current electrolysis. The duration of the electrolysis was controlled to obtain the desired thickness of polyaniline, which was generally several μm. For constructing the display devices, an amount of electricity (400 to 500 C) corresponding to the deposition of polyaniline films on SnO₂ glass was passed to obtain a film thickness of 1.5 μm to 2.0 μm. The films which were formed in 1 M HClO₄ or AlCl₃ containing 1% *p*-toluenesulfonic acid were found to be uniform and showed good electrochromism.

Results and discussion

The polyaniline films were formed by oxidation of 0.1 M aniline in 1 M AlCl₃ supporting electrolyte. Cyclic voltammetry of aniline in this electrolyte showed only one anodic peak and a corresponding cathodic peak similar to that observed in 0.1 M H₂SO₄. Upon cycling the potential between -0.2 V and 1.0 V, a good polyaniline film was obtained on the working electrode. The cyclic voltammogram of polyaniline film in AlCl₃ supporting electrolyte (with no aniline in the medium) is shown in Fig. 1. With a SnO₂ glass electrode, the cyclic

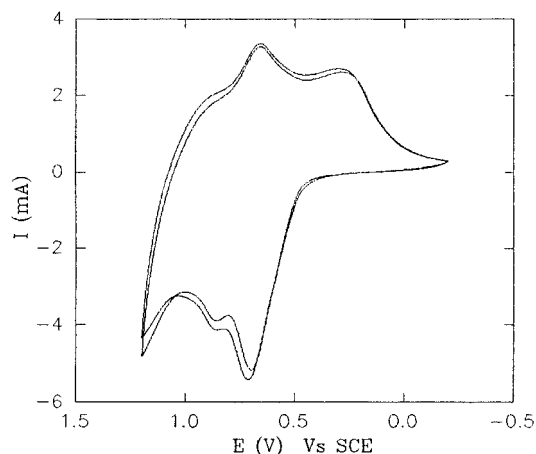
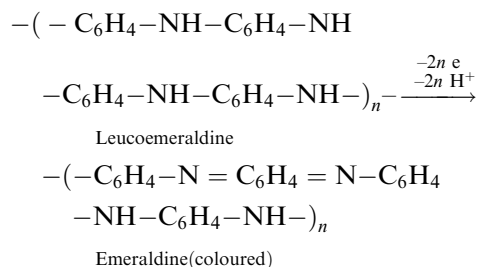


Fig. 1 Cyclic voltammetric curve of polyaniline film on SnO₂ glass as the working electrode, Pt plate as the counter electrode and SCE reference electrode. Medium: 1 M AlCl₃

voltammetric curve exhibited identical features to those observed with a Pt electrode. The potential excursions from 0 to 1.0 V produced sharp colour changes on the electrode from colourless to green, suggesting that surface activity is helpful for the electrochromic display. The anodic peak is attributed to the reaction



Potential step electrolysis for display device

The potentiostatic deposition of polyaniline was carried out in AlCl₃ (or in 1 M HClO₄) electrolyte containing 0.1 M aniline and 1% *p*-toluenesulfonic acid by stepping the potential of the working electrode to 1.0 V vs SCE using SnO₂ glass electrodes. An increase in current flow was observed during the oxidation of aniline in contrast to the normal diffusion-controlled oxidation for a fixed area of the working electrode. This current increase is attributed to the increased surface area of the working electrode caused by the uniform deposition of polyaniline. The polyaniline film formed on the substrate produces the cyclic voltammetric features identical to the one described in the previous section in the AlCl₃ electrolyte.

The electrical conductivity of the polyaniline film deposited on SnO₂ glass was measured by the four-probe method [4]. This substrate was chosen for the electrochromic display as it transmits visible wavelength radiation. For electrical contact a strip of Ag was vacuum

deposited over one end of the polyaniline-coated SnO₂ glass plate. The average conductivity of the film was 10 S/cm.

Electrochromic display

The electrochromic display was constructed with SnO₂ glass coated with polyaniline and bare SnO₂ glass using viscous AlCl_{3(aq)} electrolyte [5]. This electrolyte acts as a Lewis acid in the reactions discussed earlier. It forms a melt by absorbing water (2.75 times the weight of AlCl₃). To optimise the performance of the electrochromic glass, the conductivity of the AlCl_{3(aq)} electrolyte was measured as a function of the added water per gram of AlCl₃; the plot of conductivity as a function of the added water is shown in Fig. 2. It reached a maximum value at 5 ml water/g AlCl₃. This composition was used in the construction of the display device. When the display was constructed by spreading the electrolyte on polyaniline-coated SnO₂ glass and superimposing another SnO₂ glass, the display functioned for a short period (30 min) upon voltage reversals (−0.5 to 1.5 V). With time, the evolution of hydrogen at the cathode produced bubbles in the display. This problem was overcome by adding 5 ppm Ag ion to the electrolyte medium. This appeared to form a complex with the basic electrolyte, which inhibited the discharge of hydrogen by preferential deposition. The long-term stability of the display device was obtained by using this electrolyte; for testing the performance, the display was set for 60 s at a positive potential of 2.5 V (appearance of dark green) followed by an equal duration at a negative potential of −0.5 V (appearance colourless). Defining this as one cycle, the cycle life for 1000 repetitions was determined. The cyclic voltammetric behaviour of polyaniline before and after 1000 cycles showed a difference of only about 6%. The display reactions at the positive electrode are represented by Eq. 1, while reduction of Ag⁺ takes place at the negative electrode.

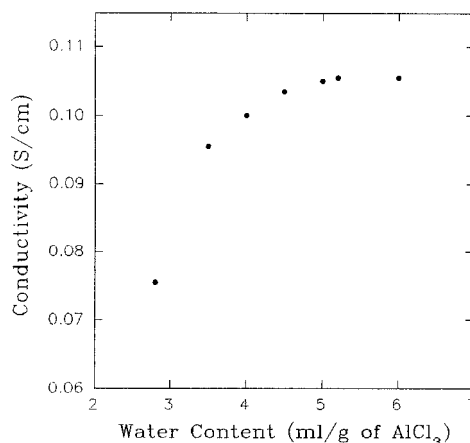


Fig. 2 Plot of electrolytic medium conductivity of AlCl_{3(aq)} melt as a function of added water per gram of AlCl₃ in the display device

The shelf life of the display was determined for a period of 1 month. The cyclic voltammetric and potential step behaviour remained identical. The response time was measured by placing the device in an He-Ne laser path and monitoring the output with a fast-rise photodiode. The response time for the electrochromic display device was estimated at about 10 ms.

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