

Electrochemistry of Polyaniline: Study of the pH Effect and Electrochromism

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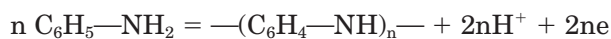
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ABSTRACT: Polyaniline was electrochemically synthesized from an aqueous medium with various acid electrolytes via potentiodynamic and potentiostatic techniques. The electrochemical synthesis of polyaniline was studied over various substrates, including Pt, Ti, Ni, and SnO₂ coated glass, and in various acid electrolytes. Cyclic voltammograms of electrochemically synthesized polyaniline were studied in HCl in a pH range of 1–4. Probable electrochemistry and chemical changes were deduced that occurred when polyaniline film was electrochemically oxidized and reduced between –0.2 and 1.0 V versus a Ag/AgCl reference electrode in an acidic electrolyte at pH 1, and three corresponding oxidation and reduction peaks were described instead of two redox peaks (as observed by W. S. Huang, B. D. Humphrey, and A. G. MacDiarmid, *J Chem Soc Faraday Trans 1* 1986, 82, 2385). The electrochromic property was studied with changes in the chemical states of polyaniline during electrochemical oxidation and reduction. A new viscous electrolyte, aqueous AlCl₃ (pH 2), saturated with AgCl was used for the construction of an electrochromic display device. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 378–385, 2002

Key words: electropolymerization; conducting polymers; polyaniline; electrochromism; cyclic voltammetry; potentiostatic technique

INTRODUCTION

Polyaniline can be produced through the anodic or chemical oxidation of aniline monomer. The electrochemical polymerization of aniline may be represented with a general stoichiometry



in which electrons are extracted from aniline by the anode during electrolysis.

Despite MacDiarmid et al.'s¹ description of polyaniline as a novel conducting polymer in

1986, the electrochemical preparation of polyaniline dates back to Lethby's² work in 1862. Lethby described dark-green polyaniline that precipitated on an electrode surface when aniline was oxidized electrochemically in a dilute sulfuric acid solution. Later, in the 1960s, the electrochemical oxidation of aniline and, therefore, the preparation of polyaniline were studied extensively by Mizoguchi and Adams.³ The latter polyaniline was extensively investigated by several researchers. The electrochemical oxidation of aniline has typically been carried out in aqueous electrolytes galvanostatically,^{4–10} potentiostatically,^{11–14} or through the cycling of the potential (potentiodynamic) of the substrate anode (e.g., between –0.2 or 0.0 V and +0.8 V versus saturated calomel electrode (SCE) in 1M HCl,^{11,15} 0.1M H₂SO₄,¹⁶ or 1M H₂SO₄).¹⁰ Several electrolytes have been suc-

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cessfully used for the synthesis of polyaniline (e.g., HClO_4 ,^{4,5,8,14} HCl ,^{11,15} H_2SO_4 ,^{10,12,13,17,18} CF_3COOH ,¹⁸ and HBF_4).⁶⁻⁸ The polymer has been deposited on substrates ranging from the metals Au,^{7,18,19} Pt,^{4,8,15,17,18} Pt-coated Ti,⁸ and stainless steel^{14,17,20} to SnO_2 ^{11,15} and carbon.^{6,10,12,13,17,19,21,22}

Polyaniline preparation via the chemical oxidation of aniline has also been investigated.^{17,23-25} The oxidative polymerization of aniline in an acid produces the protonated, partially oxidized form of the polymer,²⁴ which can be converted to the corresponding base by treatment with an alkali solution.²⁵

Early studies of polyaniline films used cyclic voltammetry techniques for the characterization of their electrochemical properties, and its redox chemistry was found to be reversible.^{3,26,27} An interesting color-change property of polyaniline has been observed during oxidation and reduction cycles. This electrochromic property of polyaniline has been studied in several electrolytes, and a color change from light yellow to violet has been observed in electrochemical cells.^{1,27} The electrochromic response time of polyaniline on glass coated with a gold substrate has been investigated in an electrochemical cell with 2M H_2SO_4 as the electrolyte.¹⁵ The switching speed of doping to undoping for polyaniline has been estimated to be in the range of a few seconds to 10^{-3} s; for obtaining these switching speeds as well as a long number of cycles, a suitably thin protonic activity medium with high conductivity is necessary. A liquid electrolyte such as an acid would not be acceptable for several practical applications, so in this article a new electrolyte is used for developing a practical portable electrochromic display device with D-cells.

The effects of various experimental parameters, such as pH, temperature, and aniline concentration, on polyaniline properties have been studied by a number of investigators.²⁸⁻³⁴ One of the most interesting parameter effects, that of pH, on the electrochemical properties of polyaniline has been intensively investigated, and its chemical changes are related to the potential change during the oxidation and reduction steps.^{1,2} Earlier workers^{1,2} tried to investigate the various chemical changes during the electrochemical reaction when polyaniline-coated electrodes were cycled between -0.2 and 0.8 V versus SCE. Five chemical states of polyaniline were investigated, but only two oxidation and reduction peaks were resolved from the voltammogram of polyaniline¹ corresponding to the five chemical states. In this work, the various chemical states

of polyaniline are correlated with the voltammogram of electrochemically deposited polyaniline with three reversible redox peaks, and the change in the pH effect is also studied from pH 1 to 4. An electrochromic display device with a novel electrolyte is also reported that is based on an intensive study of the pH effect and electrochromic property of electrochemically polymerized polyaniline.

EXPERIMENTAL

Reagents

Aniline (SRL Chemicals, Mumbai, India) was purified by distillation, and the fraction (colorless) boiling at 80°C was used for the formation of the polymer. AlCl_3 , trichloroethylene, acetone, HClO_4 (S.D. Fine Chemicals, Mumbai, India), *p*-toluene sulfonic acid (Koch-Light, Ltd., New York), H_2SO_4 , and HCl (BDH, Mumbai, India) were used without any purification. All the other chemicals were analytical-grade.

Electrodes

Pt, Ni, Ti, and SnO_2 coated glass electrodes ($1\text{ cm} \times 1\text{ cm}$) were used as working electrodes for deposition and for recording the behavior of polyaniline. All the electrodes (except SnO_2) were polished with emery paper, from 200 mesh to $1\text{-}\mu\text{m}$ diamond paste and $0.5\text{-}\mu\text{m}$ silicon gel on a velvet cloth. The electrodes were etched with either 20% HCl or 40% $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$ (1:4:6) for 20–30 s. SnO_2 glass plates were cleaned by sonication in trichloroethylene followed by washing in acetone and distilled water. For recording the cyclic voltammetry, a Ag/AgCl (Orion, Orion, Beverly, MA) reference electrode was used. Pt mesh ($2\text{ cm} \times 2\text{ cm}$) was used as the counter electrode. For a large display, a SnO_2 glass plate ($7\text{ cm} \times 5\text{ cm}$) was used as a working electrode. All the electrochemistry was done with a PAR 273 potentiostat/galvanostat (Princeton Applied Research, Princeton, NJ) in conjugation with an Omniograph (Houston Instruments, Houston, TX) x-y recorder and a 757 VA Computrace computer interface (Metrohm, Herisau, Switzerland).

Polyaniline Deposition

Polyaniline was deposited by either potentiodynamic (sweeping the potential) or potentiostatic (constant potential) techniques.³⁵ The coulombs that passed in the electrolysis were controlled to

obtain the desired thickness of polyaniline. Polyaniline was deposited electrochemically on the various substrates, Pt, Ni, Ti, and SnO₂ coated glass plates, from various acidic electrolytes (1M) such as HCl, HClO₄, *p*-toluene sulfonic acid, and H₂SO₄ (0.5M) with typical concentrations of 0.1M aniline. Polyaniline was synthesized under potentiodynamic conditions by the potentials of substrates being cycled between -0.2 and 1.0 V versus Ag/AgCl for 100–150 cycles at a 100 mV/s scan rate and under potentiostatic conditions by the potential being kept at 1.0 V versus Ag/AgCl at 25°C for a sufficiently long time to get the optimum thickness.

For constructing the large display, polyaniline film was formed potentiostatically at 1.0 V versus Ag/AgCl from 1M HClO₄ and a 0.1M aniline solution by the passage of nearly 400–500 C over a SnO₂ glass plate (7 × 5 cm²).

Cyclic Voltammetry Studies

Cyclic voltammetric studies of polyaniline film derived electrochemically over a Pt electrode was performed in HCl at various pHs. The redox property, different chemical states, and electrochromic property of the polyaniline film were studied during the cycling of the potential between -0.2 and 1.0 V versus Ag/AgCl in HCl at pH ranging from 1–4 at 25°C. Voltammograms were recorded at pH 1, 2, 2.5, 3, and 4 in HCl and also in aqueous AlCl₃ electrolyte (absence of Ag⁺ ions). Dry AlCl₃:H₂O in a 1:2.75 (v/v) ratio was used as a viscous electrolyte of pH 2 for studies of the redox property of the polyaniline film over metal electrodes and SnO₂-coated glass plates.

Electrochromic Display

An electrochromic display device was constructed with a pair of SnO₂-coated glass plates (7 cm × 5 cm) with an electrical connection at their one edge. Polyaniline was coated over one SnO₂ glass plate from 1M HClO₄ and a 0.1M aniline solution by potential step electrolysis at 1.0 V versus Ag/AgCl by the passage of 400–500 C of current. A polyaniline-coated SnO₂ glass plate was washed under a flow of water to remove aniline and oligomers. AlCl₃:H₂O (1:2.75) saturated with AgCl was used as a viscous electrolyte; it was smeared over the polyaniline-coated SnO₂ glass plate, and a second SnO₂ glass plate was placed over it without any air bubbles being trapped inside. All four edges were covered with Teflon tape. The electro-

chromic display was operated by the application of the potential from a Ni–Cd rechargeable dry cell in three steps of -0.5, 0, and 1.2 V. Ultraviolet–visible spectra were recorded for the electrochromic display during the three potentials steps. The electrochromic display was used for 100 cycles (over a period of 15 days) of the potential steps -0.5, 0, and 1.2 V with a 60-s retention time in each step without any evolution of the gas bubbles or evaporation of the electrolytes.

RESULTS AND DISCUSSION

Potentiodynamically, polyaniline was deposited over a Pt electrode from various acid solutions, including 1M HClO₄, 0.5M H₂SO₄, 1M HCl, and a 1M aqueous solution of *p*-toluene sulfonic acid containing 0.1M aniline, by the cycling of the potential (for 100 cycles) of the substrate between -0.2 and 1.0 V versus Ag/AgCl at a 100 mV/s scan rate, and voltammograms are recorded as shown

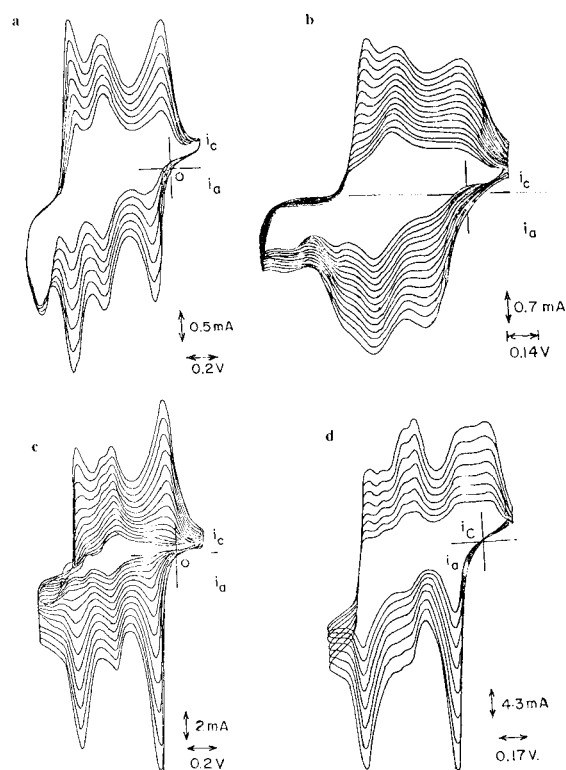


Figure 1 Cyclic voltammograms of polyaniline formation in (a) 1M HClO₄, (b) 0.5M H₂SO₄, (c) 1M HCl, and (d) a 1M aqueous solution of *p*-toluene sulfonic acid containing 0.1M aniline through the cycling of the potential of the Pt working electrode between -0.2 and 1.0 V versus Ag/AgCl at a scan rate of 100 mV/s at 25°C.

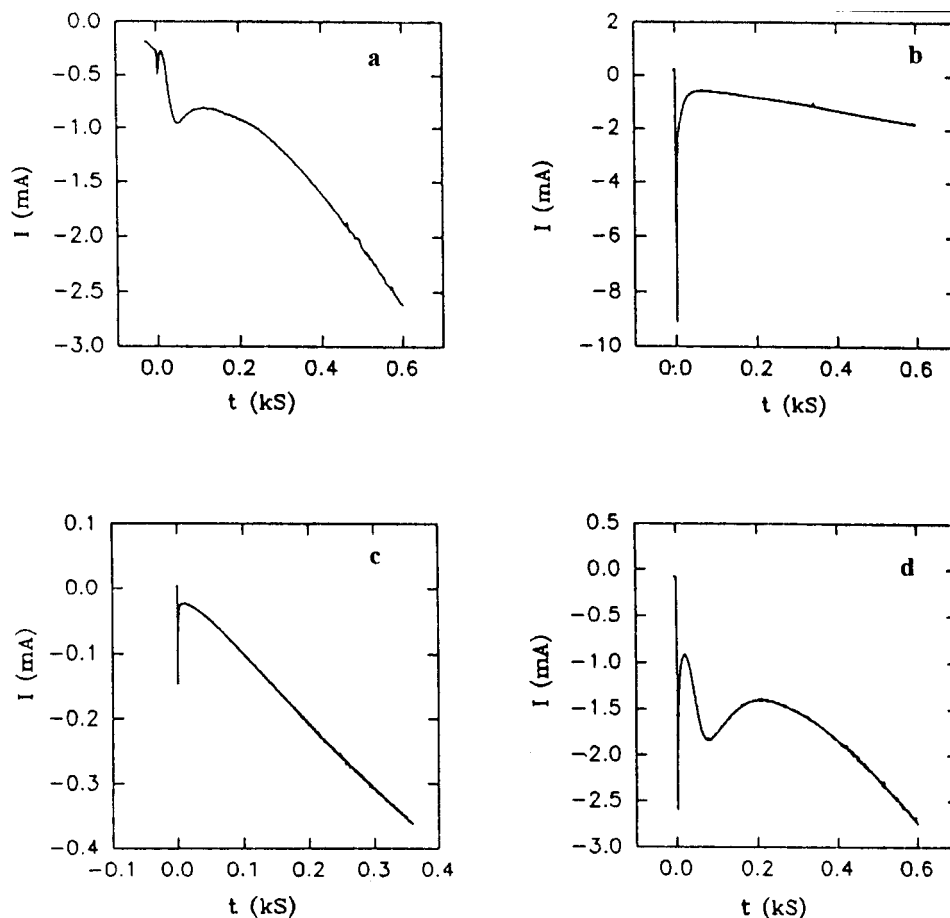


Figure 2 Potentiostatic depositions of polyaniline at 1.0 V versus Ag/AgCl in 1M HClO₄ containing 0.1M aniline on different substrates at 25°C: (a) Ni, (b) Pt, (c) SnO₂, and (d) Ti.

in Figure 1(a–d) (recorded after a few cycles), respectively. The three oxidation peaks *a*, *b*, and *c* and the corresponding three reduction peaks *a'*, *b'*, and *c'* were observed in all the acidic media except 0.5M H₂SO₄, where *b* and *c* merged, which might have been due to the relatively higher pH of the electrolyte. The lower potential redox peak *a/a'* can be attributed to a reversible reaction of aniline radical cations, and the *b/b'* redox peaks are attributable to benzoquinone/hydroquinone couple formation in the acid electrolyte.²⁶ The highest oxidation potential peak *c* and corresponding reduction peak *c'* suggest an accumulation of the oxidation product on the surface that varies with the concentration of aniline as well as the scan rate of the potential cycles.²⁶ All three peaks were well resolved and defined in 1M HClO₄, and the film formation was found to be best in this electrolyte.

The potentiostatic deposition of polyaniline was carried out in 1M HClO₄ containing 0.1M

aniline by the stepping of the potential of the working electrode to 1.0 V versus Ag/AgCl over Pt, Ni, Ti, and SnO₂ glass electrodes. The current–time curves for the deposition of polyaniline are shown in Figure 2(a–d) for Ni, Pt, SnO₂ glass, and Ti electrodes, respectively, with an increase in the surface area and the uniform deposition.

The cyclic voltammetric curves of polyaniline deposited on a Pt electrode (1M HClO₄ and 0.1M aniline) by the cycling of the potential between –0.2 and 1.0 V versus Ag/AgCl at a scan rate of 100 mV/s) were recorded in HCl in the pH range 1–4 and are shown in Figure 3(a–d). At pH 1.0, three reversible anodic peaks, *a*, *b*, and *c*, and their corresponding reduction peaks, *a'*, *b'*, and *c'*, were observed. With the increase in the pH, the *c* and *c'* peaks shift toward lower potential values, and as the pH of the medium is increased, there appears only one broad anodic peak as well as a cathodic peak (pH 4), whereas no peak shift was observed for *a/a'* and *b/b'* with changes in the pH range 1–4.¹ A

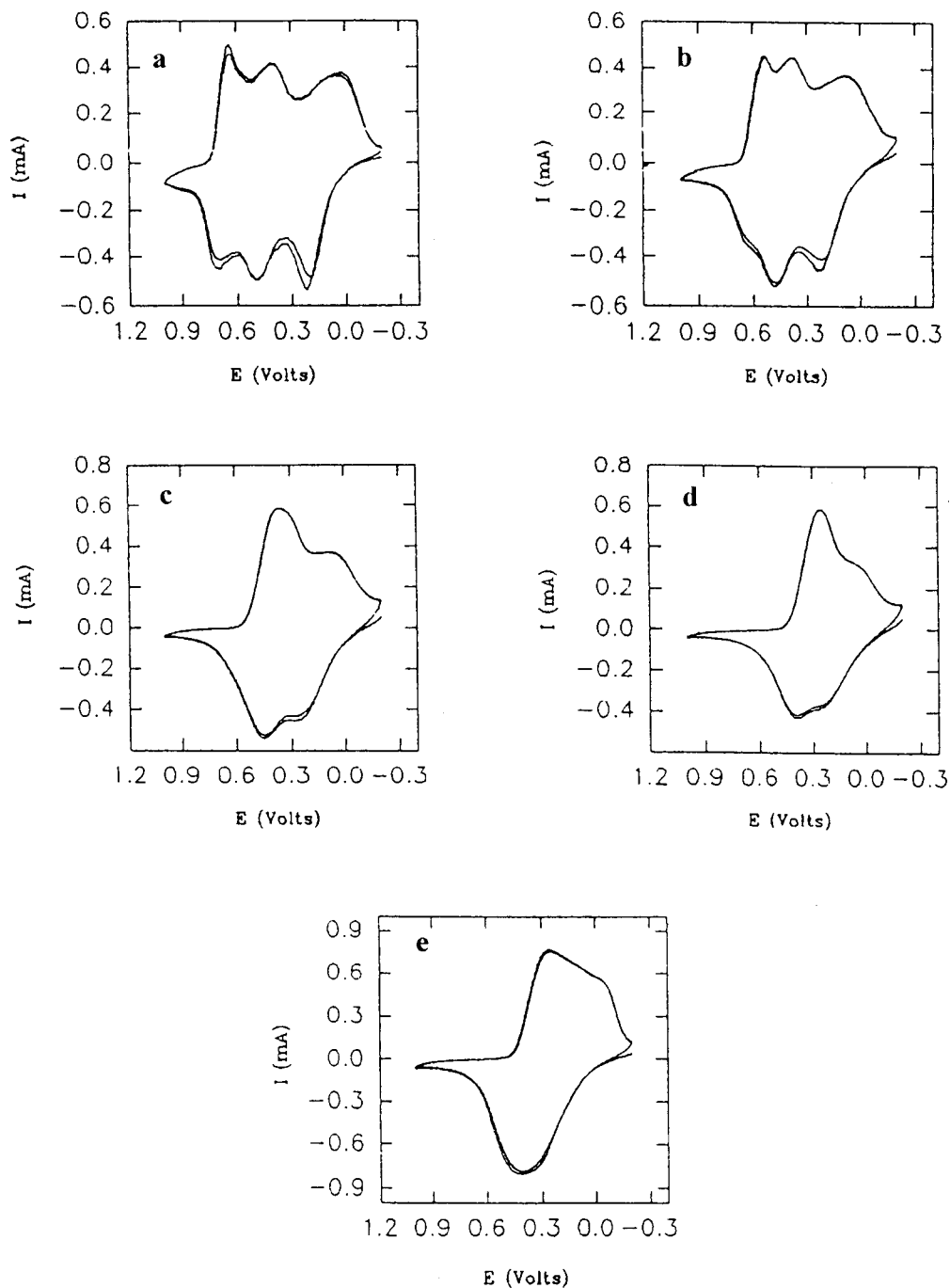
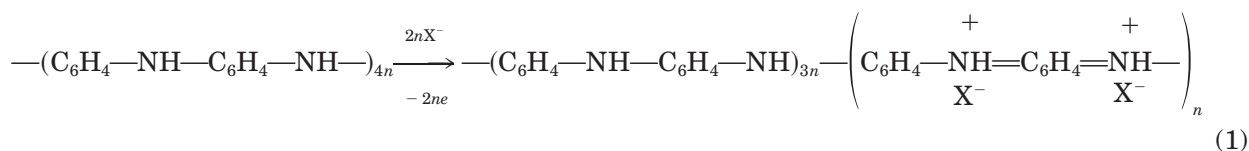


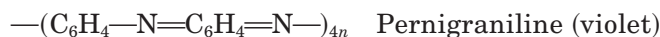
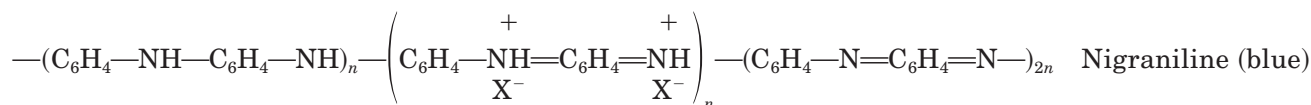
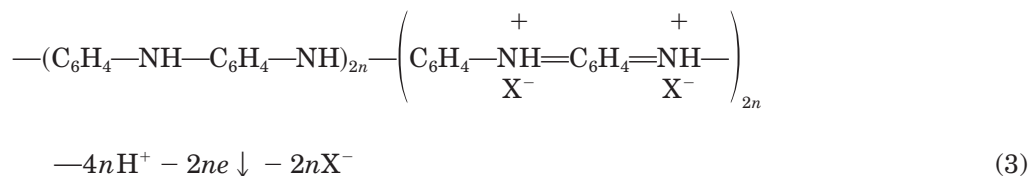
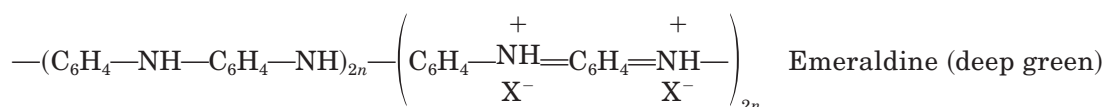
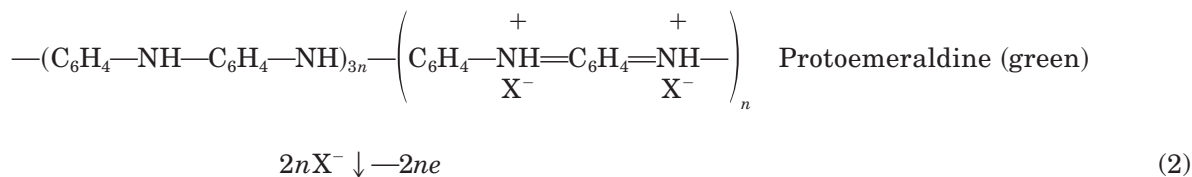
Figure 3 Cyclic voltammograms of polyaniline films recorded in three electrodes—a single-compartment cell with Pt as the working electrode, Pt gauze as an auxiliary electrode, and Ag/AgCl as the reference electrode at a scan rate of 20 mV/s in HCl—at pHs of (a) 1, (b) 2, (c) 2.5, (d) 3, and (e) 4.

fast and good change in color from light yellow to violet was observed for polyaniline film up to pH 2.5, whereas above this pH, the change in color was very poor and not very distinguish-

able. The effect of pH on the electrochemical and electrochromic properties of polyaniline may be attributed with the following probable reactions, which occur at various potentials:



Leucoemeraldine (light yellow) $\text{X}^- = \text{anion as a dopant}$



The observed peaks a/a' and b/b' in the cyclic voltammogram (at pH 1) are probably caused by reactions (1) and (2).¹ This reaction involved only the transfer of the electrons; no proton is involved in the redox reaction. Therefore, both peaks are pH-independent. The peak c/c' is probably responsible for reactions (3) and (4), in which protons are involved in the redox reactions; therefore, the peak is pH-dependent.¹ The pernigraniline state is a fully oxidized state of the polyaniline chain that occurs at a higher potential, and degradation of the chain is quite possible. The peaks c and c' shift toward lower potential values as the pH of the medium is increased, and at pH, 4 the peaks merge with the lower potential peaks in one broad peak. At the higher pH, the change in colors is not distinguishable, and the response time is slow, as evident from the

redox peaks above pH 2. An electrochromic display was constructed that was based on these studies of the effect of pH on color changes in polyaniline film. The problems associated with common acid electrolytes are hydrogen evolution at higher potentials (>1.0 V), electrolyte resistance, and evaporation of electrolytes during the cycle of the potential. These problems were resolved with a unique electrolyte, $\text{AlCl}_3:\text{H}_2\text{O}$ (1:2.75), saturated with AgCl. Dry AlCl_3 (1.0 g) was dissolved in 2.75 mL of H_2O to obtain a viscous solution of pH 2 having optimum conductivity and saturated with AgCl crystals. A cyclic voltammogram for a polyaniline-coated SnO_2 glass plate was recorded in the aforementioned electrolyte of $\text{AlCl}_3:\text{H}_2\text{O}$ (1:5) in a three-electrode single-compartment cell with a Pt auxiliary and Ag/AgCl reference electrodes. Figure 4(a,b) shows voltam-

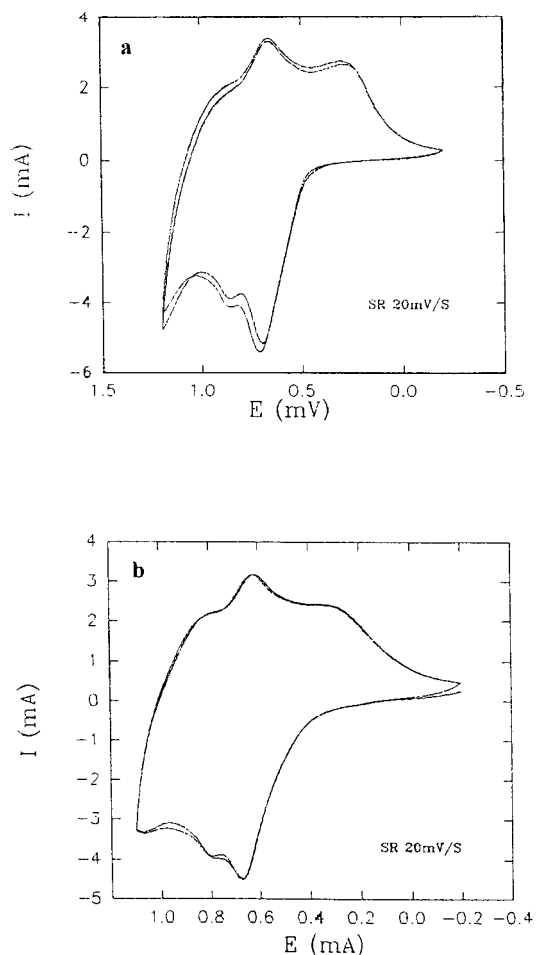


Figure 4 Cyclic voltammograms of polyaniline films in aqueous AlCl_3 electrolyte: (a) just after formation over a SnO_2 -coated glass plate from 1M HClO_4 containing 0.1M aniline and (b) the 99th and 100th cycles after 15 days.

mograms for the 1st and 2nd cycles and the 99th and 100th cycles of polyaniline (recorded over 15 days) in the potential range of -0.2 to 1.2 V at a 20 mV/s scan rate. Cyclic voltammograms show two redox peaks at higher potentials in comparison with other acid electrolytes. A negligible loss of polyaniline over the period of 15 days after 100 cycles is revealed, and the electrochromic property of polyaniline is the same as for the other acid electrolytes. A sharp and fast change in the color from light yellow to black-blue for polyaniline film can be observed in this electrolyte from -0.2 to 1.2 V. The aqueous AlCl_3 electrolyte (1:5) was found to be acidic in nature (pH 2), probably because of the formation of $\text{Al}(\text{OH})_3$, Cl^- and H^+ . The electrolyte behaved nearly the same as HCl (pH 2), except for a certain difference due to the

formation of gelatinous $\text{Al}(\text{OH})_3$, which has low dissociation. Therefore, the electrochemistry of polyaniline is not much different, and the dopant is the same as Cl^- , although some effect on the electrochemical behavior of polyaniline may be attributed to a change in the mobility of dopants in the dense gelatinous electrolytic medium and the dissociation of $\text{Al}(\text{OH})_3$.

An electrochromic display was constructed with a pair of SnO_2 -coated glass plates ($7\text{ cm} \times 5\text{ cm}$) and the aforementioned electrolyte. Ultraviolet-visible spectra were recorded for the electrochromic display during the three potential steps of -0.5 , 0.0 , and 1.2 V, each 60 s long, as shown in Figure 5(a–c), respectively. The electrochromic display was light yellow with nearly 70 – 80% transparency at -0.5 V, blackish blue with nearly 20 – 30% transparency at 1.2 V, and in an intermediate state of green at 0 V. The display was operated with a Ni–Cd rechargeable dry cell for several cycles without any gas bubbles or evaporation of electrolyte. The inhibition of the discharge of hydrogen in this electrolyte was probably by preferential deposition of Ag^+ over the cathode, and the hydrogen evolution potential was higher in this electrolyte in comparison with that of other acid electrolytes. The loss of water during the large number of display cycles was minimized because of very low resistance between the SnO_2 plates and, therefore, low heat generation and because AlCl_3 is highly hygroscopic in nature, so if any water loss took place, it was recovered from the environment.

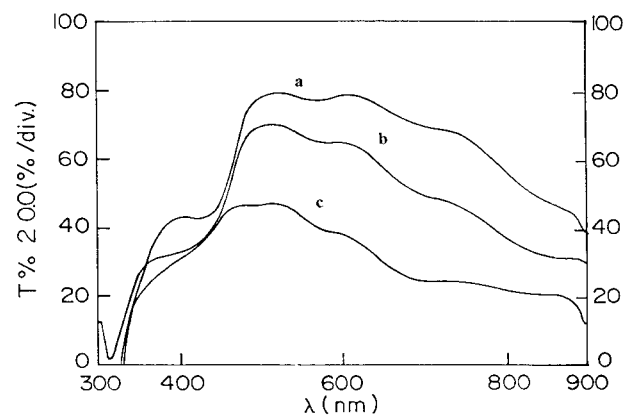


Figure 5 Ultraviolet-visible spectra of the large electrochromic display during the three potential steps: (a) -0.5 , (b) 0.0 , and (c) 1.2 V (each for a 60 -s time period).

CONCLUSIONS

Polyaniline was synthesized over a number of substrates through various acid electrolytes with potentiostatic and potentiodynamic techniques. The fast growth and good quality of the polyaniline film formation was observed in 1M HClO₄ containing a 0.1M aniline solution. Polyaniline was characterized electrochemically in HCl electrolyte at various pHs. The various probable chemical reactions and states of polyaniline were explained with respect to three redox peaks observed during its cyclic voltammetry at pH 1. The change in the color of the polyaniline film was related to its various states and also studied in the pH range 1–4. The electrochromic property of polyaniline was used for the construction of a large display device with a pair of SnO₂ glass plates and a new AlCl₃ electrolyte to overcome the problems associated with common acid electrolytes. The electrochemical behavior of polyaniline in this new electrolyte was found to be the same as for other acid electrolytes. The electrochromic display constructed with AlCl₃ aqueous electrolyte was successfully displayed for a large number of cycles in the potential range –0.5 to 1.2 V with a dry Ni–Cd battery.

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