Effect of electrolytes on electrochromic properties and morphology of poly(2,5-dimethoxy aniline) films

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Abstract. Poly(2,5-dimethoxyaniline) (PDMA) was electrochemically synthesized in oxalic ($H_2C_2O_4$) nitric (HNO_3) and hydrochloric (HCl) acids and deposited onto flexible indium tin oxide at various synthesis times and deposition potentials as electrochromic materials. The PDMA films were characterized by FT–IR-spectrometry, scanning electron microscopy, UV–Vis spectrophotometry and cyclic voltammetry. All PDMA films show reversible colour changes from yellow to green corresponding to the transition from the fully reduced state to the fully oxidized state under potential switching. The surface morphology and thickness of PDMA films depend critically on the type of acids used in the electrochemical polymerization process. The morphology of PDMA are highly porous microfibres ($H_2C_2O_4$ and HNO_3), tiny granular aggregate (HCl) and particle agglomerate depending on the polymerization time. The fastest response time observed via colour changing of 3·7 s is obtained from the HCl–PDMA film at 3·5 volt and at the synthesis time of 6 min, as primarily due to the thickness of the film. The flexible PDMA film is demonstrated here as a potential candidate to be used in electrochromic devices.

Keywords. Electrochromic polymer; poly(2,5-dimethoxyaniline); electrochemical polymerization; response time.

1. Introduction

Conductive polymers continue to gain growing interest, because they are widely used in many applications: optical displays, rechargeable batteries, electrochromic devices and light emitting diodes (Ramakrishnan 1997). Among organic molecules, conductive polymers have attracted significant interest in the field of electrochromism.

Electrochromism is defined as a reversible and visible change in its transmittance and/or reflectance of electrochromic materials as a result of an oxidation–reduction reaction. The applications for such materials are mirrors of vehicles (Sonmez 2005), smart windows (Kim *et al* 2009), electrochromic displays (Bange 1999), earth-tone chameleon materials (Brotherson *et al* 1999), ink-jet printers and most recently E-paper (Peters and Freeman 1991).

Earlier reports (Sonmez 2005) indicated that the use of inorganic compounds or the metal oxides, iridium dioxide (IrO_2) and tungsten trioxide (WO_3), which were mixed-valence metal complexes. However, these transition metal oxides electrochromically exhibited a slow response time (tens of seconds) and a high processing cost. Compared

with electrochromic polymers, they have several merits: low processing cost, low power requirement during switching, low operating voltage, repeatability, high colouration efficiency, good UV stability, fast switching ability and fine-tuning ability of the band gap via modification of chemical structure of the polymer. Additionally, there is no dependence on the angle of vision (Sonmez 2005).

Potential conducting polymers are comprised of a number of functionalized groups such as polypyrroles, polythiophenes, polyanilines, etc. (Sapp *et al* 1998). They have been recognized as an interesting class of electrochromic materials. An important issue of electrochromic polymers has been that of controlling their colours by main-chain and pendant-group structural modifications.

Polyaniline (PANI) is one of the most promising conducting polymers due to an easy polymerization process and excellent chemical stability, combined with relatively high levels of conductivity (Khan *et al* 2003). Poly(2,5-dimethoxyaniline), or PDMA, is the derivative of PANI which shows higher solubility and faster response time than PANI. PDMA film can make reversible colour changes from yellow to green representing a switch between the reduced state to the oxidized state through an application of electrical potential faster than that of PANI (Sun *et al* 2013). Cyclic voltammetry results have also

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confirmed that PDMA can be easily switched from the leucoemeraldine state to the emeraldine state. PDMA also shows a shorter response time (9 s) than the electrochemically prepared PANI (22 s) (Huang *et al* 2002).

Normally, the electrochromic materials are produced in the form of thin film. They can be produced by many methods including electron beam deposition, chemical vapour deposition, the Langmuir–Blodgett technique and the layer-by-layer self-assembly technique (Sarkar *et al* 2000). In the case of electronically functional thin films, thinner films are generally preferred due to the shorter electron and ion transport path length (Montazami *et al* 2010).

The purpose of this work was to polymerize 2,5-dimethoxyaniline (DMA) via electrochemical polymerization on indium tin oxide (ITO) plastic submerged in oxalic, nitric and hydrochloric acids at various synthesis times (3, 6 and 10 min) and applied potentials (1 and 1·5 V). This study was also intended to investigate the effect of various electrolytes on the electrochromic properties of PDMA film due to different doping characteristics. The PDMA films were characterized for the electrochromic properties using a UV–Visible spectroelectrometer. Fourier-transform infrared spectrometer and thermogravimetric analyser were also utilized to investigate the chemical and thermal properties of PDMA film, respectively. The morphology and thickness of the PDMA coated ITO surface were studied by scanning electron microscope. Cyclic voltammetry was used to study the oxidation–reduction properties of the PDMA/ITO plastic.

2. Experimental

2.1 *Materials*

The starting monomer, 2,5-dimethoxy aniline (DMA), was purchased from Sigma Aldrich (AR grade, 98%). Oxalic acid (Ajax Finechem, AR grade), hydrochloric acid (Lab Scan, AR grade, 37%), sulfuric acid (Lab Scan, AR grade, 98%), nitric acid (Lab Scan) and acetic acid (Lab Scan) were used for the synthesis without further purification. An ITO-coated PET substrate (60 Ω) was purchased from Sigma Aldrich.

2.2 *Electrochemical polymerization of PDMA on ITO plastic*

PDMA was electrodeposited onto the ITO plastic using potentials of 1 V and 1·5 V, in either 25 mL of 0·1 M DMA in 0·1 M oxalic acid, hydrochloric acid, or nitric acid, and at various deposition times of 3, 6 and 10 min. Stainless steel and ITO plastic were used as the counter and the working electrodes, respectively.

2.3 *Characterization of PDMA/ITO film*

Infrared absorption spectra of PDMA were taken to study the chemical structure of PDMA. A Fourier transform infrared spectrometer (FT–IR; Thermo Nicolet, Nexus 670) was used in the absorption mode with 64 scans, covering a wavenumber range of 4000–400 cm^{-1}. Optical grade KBr was used as the background material.

A thermogravimetric analyser (TGA; Perkin Elmer, TGA7) was used to study the thermal stability and to determine the decomposition temperature of PDMA. The experiment was carried out by electrochemical polymerization of the DMA monomer in each acid solution on a stainless steel electrode for 20 min. Then, the PDMA coated stainless steel electrodes were dried and PDMA was scrapped into a powder, kept at 105 °C overnight, and later used for TGA measurements. The sample (2–3 mg) was weighed and then placed it in an alumina pan and heated under nitrogen atmosphere with a heating rate of 10 °C/min from 50 to 900 °C.

The synthesized PDMA/ITO films were characterized for redox properties with a cyclic voltammetry using a multi-channel potentiostat (VMP, Bio Logic Science Instrument). Measurements were carried out in 200 mL of 0·01 M H$_2$SO$_4$ solution as the background electrolyte, assembled with a three-electrode cells consisting of a saturated calomel electrode (SCE) as the reference electrode, a stainless-steel wire as the counter electrode, with a 2 cm^2 PDMA/ITO plastic stub used as the working electrode. The cyclic voltammogram (CV) of the PDMA/ITO electrodes was measured in the potential range of –1 to +1·5 V and vs SCE. The parameters and cell characteristics were setup as follows: a scan rate (dE/dt) of 10 mV/s, dE_R = 1 mV, with an electrode surface area of 2 cm^2. A field-emission scanning electron microscopy (FE-SEM; Hitachi S4800) was used to determine morphological structure and thickness (Kang *et al* 2009) of each PDMA-coated ITO.

2.4 *Electrochromic study of PDMA-coated ITO plastics*

Optical absorption spectra as well as optical kinetic responses of the PDMA/ITO electrode polymerized with various acids, were recorded on a spectrometer (Shimadzu, UV-1800). Measurements were carried out in a cuvette cell of 1 cm path length, assembled as an electrochemical cell with PDMA film-coated ITO plastic as the working electrode and stainless-steel wire as the counter electrode, in 0·01 M H$_2$SO$_4$ electrolyte solution. The scanned wavelength range was 400–800 nm (Neves *et al* 2004). To study the effect of the applied potential on the response time, the potentials applied to the PDMA/ITO were 0·5, 1, 1·5, 2, 2·5, 3, 3·5, 4, 5 and 10 V in the 0·01 M H$_2$SO$_4$ electrolyte solution. The effect of the electrolyte concentration on the response time was studied at the applied

potential 3·5 V in various concentrations of H_2SO_4 (10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} M).

3. Results and discussion

3.1 *FT–IR spectra of PDMA/ITO film*

The spectra of PDMA synthesized in oxalic ($H_2C_2O_4$–PDMA), nitric (HNO$_3$–PDMA) and hydrochloric (HCl–PDMA) acids are shown in figure 1. The peak at ~ 3400 cm^{-1} can be attributed to the secondary N–H stretching mode for the amine functional group. The band at 1570 cm^{-1} belongs to the C=N and C=C stretching modes of the benzenoid ring. The quinoid and benzenoid peaks of PDMA at ~ 1490 and 1580 cm^{-1} cannot be clearly observed. This may be due to the overlapping with the aromatic C=C stretching bands ranging from 1400 to 1600 cm^{-1} (Neelgund *et al* 2008). The weak band at ~ 1647 cm^{-1} is indicative of the presence of the carbonyl group C=O contained in the oxalate ion (Patil *et al* 2004). The FT–IR spectrum of HNO$_3$–PDMA includes an additional peak at 1384 cm^{-1} corresponding to the nitrate group acting as a counter ion with the protonated amine (Blinova *et al* 2009). The FT–IR results suggest that the acid-doped PDMA films are in the emeraldine and pernigraniline forms. In addition, the quinoid and benzenoid peaks appear in the spectra and the dark-green synthesized PDMA films suggest the dominance of the emeraldine and pernigraniline forms of the acid-doped PDMA films.

3.2 *Thermogravimetric analysis*

Decomposition temperatures of TGA curves indicate that all PDMA samples decompose in the same three steps (Sapp *et al* 1998). The initial weight loss at ~ 130 °C is due to the loss of water bound molecules or moisture. The next weight loss for PDMA at the temperature

~ 300 °C can be attributed to the removal of the dopant anions (Neelgund *et al* 2008). The third weight loss at ~ 450 °C indicates structural decomposition of the polymer chain.

3.3 *Morphology of PDMA surface*

Morphology of PDMA is different depending on the acids used (figure 2); the type of acid plays an important role in directing the morphology or in aligning the synthesized polymer. $H_2C_2O_4$–PDMA shows a highly porous microfibre structure (Roy *et al* 2001), while the structure of HNO$_3$–PDMA becomes a more disordered microfibre. The morphology of HCl–PDMA appears as an ordered tiny-granular aggregate. This is due to the smaller doping acid size (Cl$^-$ < NO$_3^-$ < C$_2$O$_4^{2-}$); it can occupy more accessible spaces within the chain, leading to a more compact morphology, consistent with previous work (Melato *et al* 2009; Kiani *et al* 2012). Melato *et al* (2009) studied the electro-polymerization condition of poly(3,4-ethylenedioxythiophene) under different supporting electrolytes (LiClO$_4$, TBAClO$_4$ and TBAPF$_6$). The morphology of the film using LiClO$_4$ was more compact than those of the other electrolytes, because the smaller cation size (Li$^+$) was more accessible to the polymer structure. The slightly higher size of PF$_6^-$, occupied a larger space than ClO$_4^-$ leading to a less compact structure (Melato *et al* 2009). In all acids, as the polymerization continued, the surface morphology became more disordered and accompanied by particle aggregation. The polymerization time changed the morphology of the polymer film and induced particle fusion (Hernandez-Perez *et al* 2001). On the other hand, Hernandez-Perez *et al* (2001) investigated the morphology of polypyrrole (PPy) film which was prepared by potentiostatic and voltammetric methods on a platinum electrode at various electropolymerization times (50 ms, 200 ms and 5 s). The fusion of PPy cluster formed a smooth compact film (Hernandez-Perez *et al* 2001).

3.4 *Thickness of PDMA on ITO substrate*

Thickness of the PDMA films was analysed by cross-sectional FE–SEM monographs. At a longer polymerization time, the PDMA film is thicker (Kang *et al* 2009). PDMA was synthesized during the polymerization times of 3, 6 and 10 min. The thicknesses of $H_2C_2O_4$–PDMA film are 109 ± 5, 144 ± 5 and 164 ± 8 nm, respectively. The thicknesses of HNO$_3$–PDMA films are 140 ± 5, 166 ± 9, 188 ± 8 nm, respectively. The thicknesses of the HCl–PDMA films are 78 ± 3 nm and 104 ± 2 nm at 6 and 10 min deposition time, respectively. The HCl–PDMA film produces the thinnest film at the same polymerization time because of the slow polymerization rate. The slow polymerization rate is due to the lack of oxygen atoms in the acid molecules causing no oxygen linkage
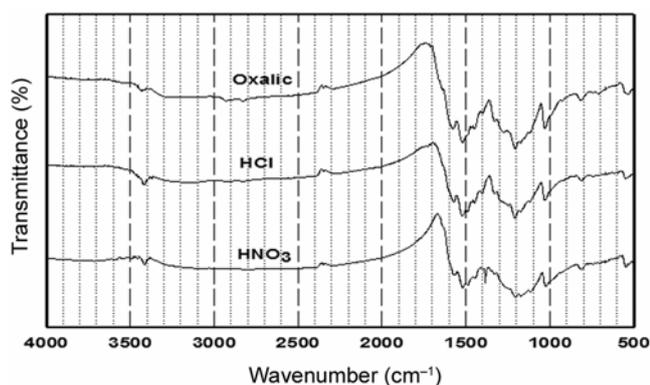

Figure 1. FT–IR spectra of PDMA film synthesized in oxalic acid, HCl and HNO$_3$ as electrolyte solutions.

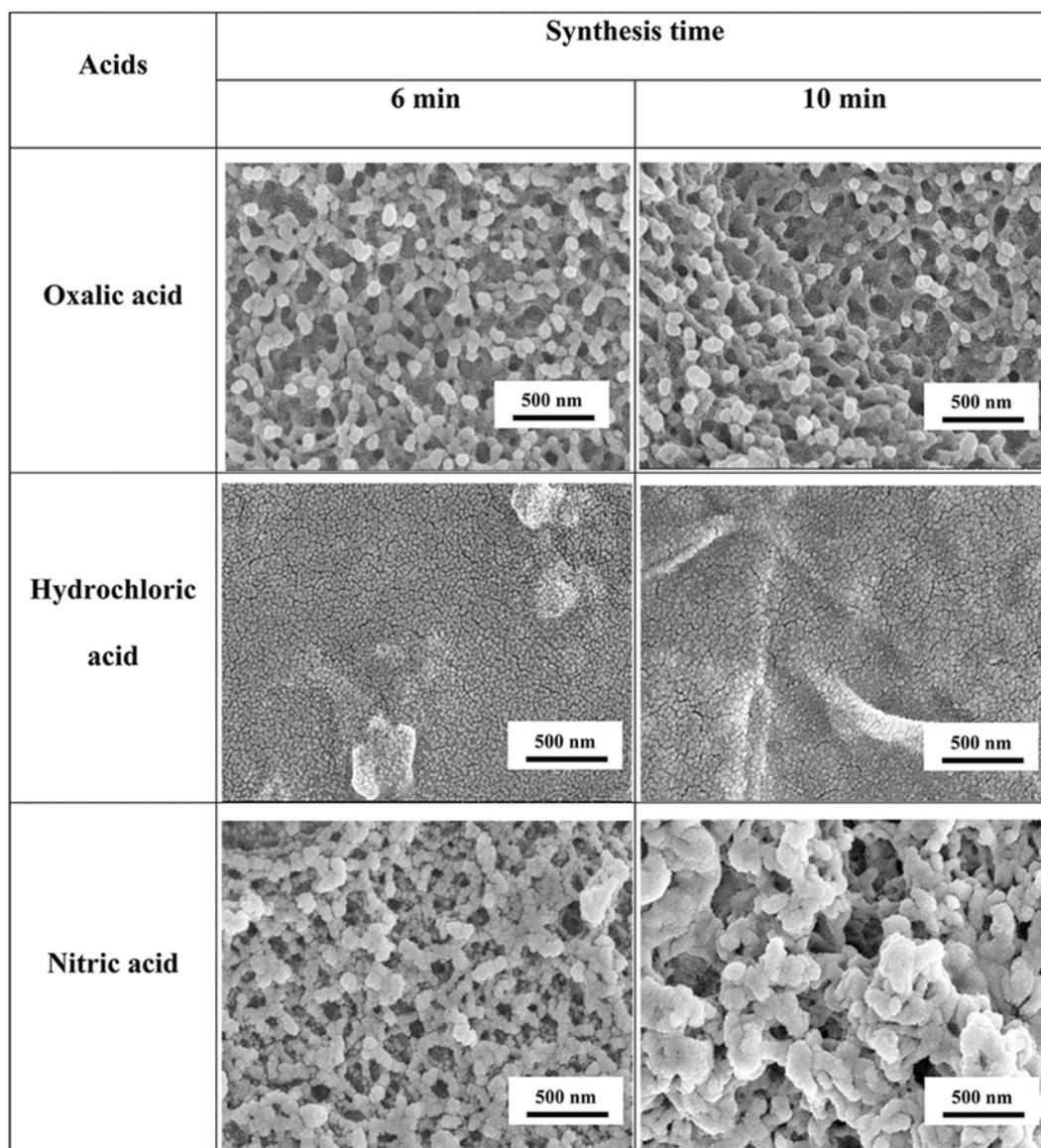| Acids	Synthesis time	
	6 min	10 min
Oxalic acid		
Hydrochloric acid		
Nitric acid		

Figure 2. Surface morphology of PDMA film synthesized in oxalic acid, HCl and HNO$_3$ as electrolyte solutions at 6 and 10 min deposition times.

between the ITO surface and the DMA monomer (Camalet *et al* 1998; Patil *et al* 2004).

3.5 *UV absorption spectrum of PDMA*

UV absorption spectra of the synthesized PDMA films, exhibit a band at $\lambda_{max} \sim 750$ nm corresponding to the pernigraniline form. At -1 V, the spectrum shows an absorption band at $\lambda_{max} = 480$ nm corresponding to the reduced state (leucoemeraldine) which disappears upon oxidation (Neves *et al* 2004; Huang *et al* 2006).

3.6 *Colouration kinetics of PDMA*

3.6a *Response and reversibility of poly(2,5-dimethoxy-aniline) film*: The absorption spectra of H$_2$C$_2$O$_4$–PDMA,

HNO$_3$–PDMA and HCl–PDMA films recorded at 1 V with 2 min interval in 0·01 M H$_2$SO$_4$ show two absorption bands at $\lambda_{max} \sim 480$ and ~ 750 nm. Figure 3(a and b) show the absorption spectra of H$_2$C$_2$O$_4$–PDMA film obtained from the oxidation and reduction reactions, respectively. The band at $\lambda_{max} \sim 480$ nm corresponds to the reduced state (leucoemeraldine). This band disappears upon an oxidation reaction, while the band appearing at $\lambda_{max} \sim 750$ nm corresponds to the oxidation state of PDMA or the pernigraniline form (figure 3a). For the reduction process, under applied potential of -1 V as shown in figure 3(b), the band at $\lambda_{max} \sim 750$ nm disappears, while the band at $\lambda_{max} \sim 480$ nm is observed, because the transformation of the oxidized pernigraniline form to the reduced leucoemeraldine form. Thus, the PDMA film can be switched from yellow (leucoemeraldine form) to blue

(pernigraniline form) and blue to yellow via the redox switching process under applied negative and positive potentials. The electrolyte type is not critical to the absorption spectra, where the absorption spectra of HNO_3–PDMA and HCl–PDMA are similar to that of $H_2C_2O_4$–PDMA, but it affects the response time.

3.6b *Effect of testing potentials on response time:* The study of the kinetic colouration of the PDMA-coated ITO electrode was carried out via the kinetic mode of a UV–Visible spectrometer. The wavelength 750 nm, representing the oxidized state, was used to identify the response time and the optical contrast between the redox states.

The effect of the testing potentials (1–3·5 V) in 0·01 M H_2SO_4 electrolyte on the reduction time, oxidation time and response time of $H_2C_2O_4$–PDMA, HNO_3–PDMA and HCl–PDMA films at various synthesis times are shown in figure 4. The reduction time, oxidation time and response time decrease with increase in the electrical potential for all PDMA samples as the increase in electrical potential induces electrical conductivity and promote the redox process colour changing mechanism (Abd-Elwahed and Holze 2002). At 6 min synthesis time, the response time of PDMA decreases from 290 to 21 s for $H_2C_2O_4$–PDMA film (figure 4a), 515 to 38 s for HNO_3–PDMA film (figure 4b) and 182 to 3·7 s for HCl–PDMA film (figure 4c) as the applied potential increases from 1 to 3·5 V. At the

10 min synthesis time, the response time of PDMA decrease from 385 to 25·5 s, 1310 to 35 s and 350 to 15 s for $H_2C_2O_4$–PDMA, HNO_3–PDMA and HCl–PDMA films, respectively (figure 4), when the applied potential increases from 1 to 3·5 V. The fastest response time of $H_2C_2O_4$–PDMA and HNO_3–PDMA films are 12·8 and 20 s, respectively, for 3 min synthesis and at the testing potential of 3·5 V (figure 4(a and b)). The faster response time for HCl–PDMA film is 3·7 s of 6 min and at the testing potential shown in figure 4(c).

The results of the response time of PDMA from various acids indicate that the increase in the polymerization time contributes to the increase in the thickness of the PDMA films and a more compact structure, resulting in slower response time. Moreover, the HCl–PDMA film shows the fastest response time (3·7 s) relative to other acids at the same synthesis time, because it produces the thinnest film and the smallest doping acid size resulting in a faster doping process (Palaniappan *et al* 2012). Furthermore, it is found that the 3·7 s response time of the HCl–PDMA is faster than the ITO/PDMA‖$LiClO_4$–PC–PEO (400,000)‖WO_3/ITO device (Huang *et al* 2002), since liquid electrolyte has greater ion mobility than gel electrolyte.

3.6c *Effect of electrolyte concentration on response time*: Since, the fastest response time for all acids was obtained at 3·5 V, this potential was used to study the effect of electrolyte concentration on response time of PDMA. In addition, the $H_2C_2O_4$–PDMA and HNO_3–PDMA films for 3 min and HCl–PDMA synthesized for 6 min showed the fastest response times, hence, these films were further used to study the effect of electrolyte concentration.

The PDMA-coated ITO plastics were tested at 3·5 V in various concentrations of H_2SO_4. Figure 5 shows that the increase in the electrolyte concentration from 10^{-6} to 10^{-2} M results in a reduction of the response time from 460 to 13·5 s, 760 to 36 s and 160 to 3·7 s for $H_2C_2O_4$–PDMA, HNO_3–PDMA and HCl–PDMA films, respectively. The HCl–PDMA film is the thinnest, consequently, it has the fastest response time. In addition, the response time decreases with increasing H_2SO_4 concentration as a higher electrolyte concentration has more protons and higher mobility, resulting in a faster response time (Zhu and Mu 2001). Ram and co-workers (1997) studied the switching response time of poly(aniline-co-*o*-anisidine) film based on the effect of HCl concentration. They showed the decrease in response time with increase in HCl concentration. Furthermore, Habib and Glueck (1989) reported that the response time of tungsten oxide film decreased with increase in $LiClO_4$ concentration. In both the cases, they explained that a higher acid concentration produced a higher amount of H^+ ion (from HCl) or Li^+ (from $LiClO_4$). The diffusion rate of H^+ or Li^+ insertion into the film played a major role in the electrochromic process.
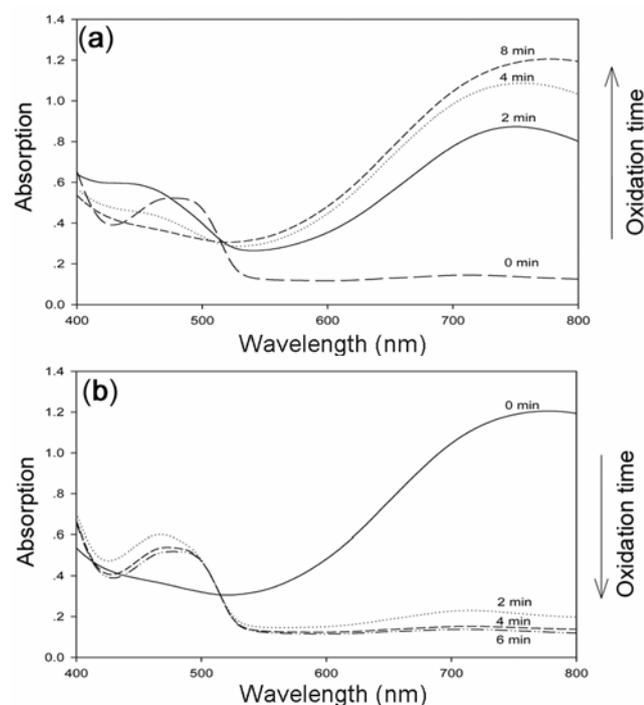

Figure 3. The absorption spectra of $H_2C_2O_4$–PDMA synthesized at 3 min deposition time in 0·01 M H_2SO_4: (**a**) oxidized state at the applied potential of +1 V and (**b**) reduced state at the applied potential of –1 V.
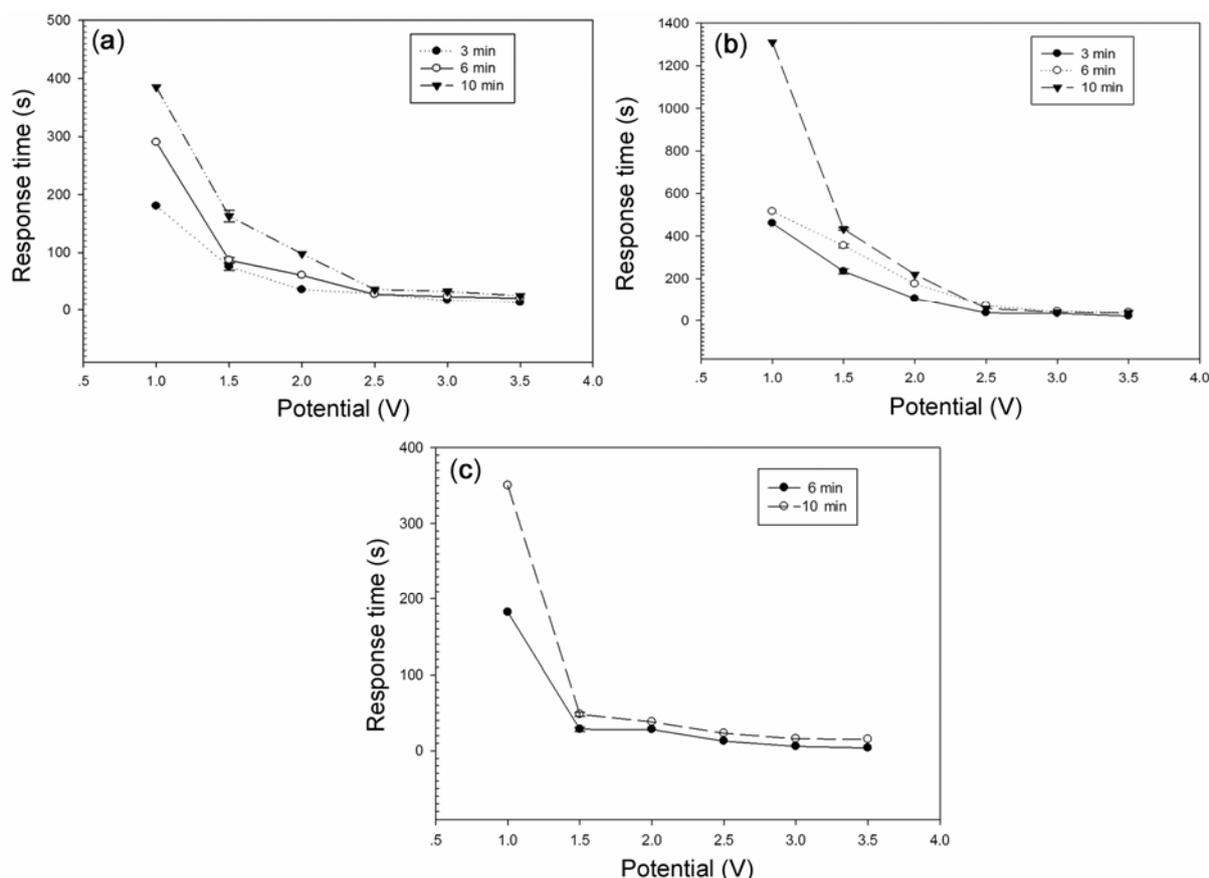
Figure 4. Effect of testing potential on response time at various synthesis times (**a**) $H_2C_2O_4$–PDMA; (**b**) HNO_3–PDMA and (**c**) HCl–PDMA.

3.6d *Effect of the type of acids and synthesis time on the optical contrast*: High optical contrast is an important property of an efficient electrochromic polymer. In this study, the optical contrast (ΔAbs) of PDMA/ITO was determined as the absorbance difference between the steady state values of the reduction and oxidation states. The optical contrasts of $H_2C_2O_4$–PDMA, HNO_3–PDMA and HCl–PDMA film at the 6 min deposition time are 0.372 ± 0.097, 1.770 ± 0.240 and 2.260 ± 0.360, respectively. At the polymerization time of 10 min, the optical contrasts of $H_2C_2O_4$–PDMA, HNO_3–PDMA and HCl–PDMA films are 1.170 ± 0.440, 2.010 ± 0.140 and 2.330 ± 0.300, respectively. The optical contrasts of the PDMA films slightly increase, when the polymerization time increases from 6 to 10 min due to increase in film thickness (Camalet *et al* 1998). PDMA synthesized at the same synthesis time shows optical contrasts in the order of nitric acid > oxalic acid > hydrochloric acid. It is evident that the optical contrast depends on the thickness of PDMA film (Camalet *et al* 1998; Holt *et al* 2005). The highest contrast between the bleached and the coloured forms is observed at $\lambda = 750$ nm ($\Delta T = 73\%$), which is higher than that of an ITO/PDMA electrode ($\Delta T = 23\%$) (Huang *et al* 2002). Kang *et al* (2009) studied the optical properties of PEDOT–PANI hybrid film based on the effect of polymerization time. The result showed that the optical contrast increased with increase in polymerization time. They explained that the polymerization time affected the film thickness and thus, the film optical contrast (Kang *et al* 2009). Holt *et al* (2005) reported the optical contrast of poly(phenylene vinylene) and PPV, based on the effects of applied voltage and salt type. The optical contrast of PPV increased with increase in applied voltage as the higher applied voltage created a greater film thickness, resulting in higher optical contrast. Furthermore, the type of anionic salt (TBA and triflate) affected the optical contrast, because it acted as a dopant (Holt *et al* 2005).

3.7 *Cyclic voltammetry (CV) of PDMA*

All PDMA films deposited on ITO show two main redox processes in which the first peak indicates the oxidation as related to the leucoemeraldine/emeraldine (yellow to green) transformation, and the second sharp peak corresponds to the emeraldine/pernigraniline (green to blue) transformation, consistent with previous studies (Gazotti *et al* 1997; Klink *et al* 2011).

Cyclic voltammograms (CV) of $H_2C_2O_4$–PDMA at various times are shown in figure 6. The $H_2C_2O_4$–PDMA film synthesized at 10 min shows two redox peaks at –0·35/–0·85 and 0·95/1·00 V (E_{pa}/E_{pc}). There are two reduction peaks which appear at 0·80 and 0·85 V for $H_2C_2O_4$–PDMA film synthesized at 6 min and 0·65 and 0·90 V for $H_2C_2O_4$–PDMA film synthesized at 3 min. The oxidation peaks appear at –0·55 and –0·40 V for the 6 and 3 min deposition times, respectively. In this work, it is difficult to observe two oxidation peaks because of the anionic effect (Palys *et al* 2000) hindering the polymer oxidation by the large anion ($C_2O_4^{2-}$) resulting in the board peak as previously shown by Palys *et al* (2000). Furthermore, they reported the shapes of PDMA cyclic voltammograms strongly depended on the anion type (ClO_4^-, SO_4^-, Cl^- and $CClO_3COO^-$). The oxidation peak current increases, while the reduction peak current decreases with increasing polymerization time, resulting
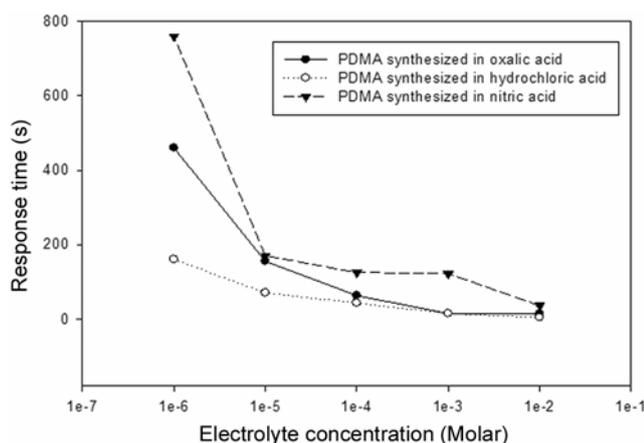
in the expansion of the current–potential curve area due to the increase in film thickness or a higher specific capacitance (Chiu *et al* 1992; Sun *et al* 2013). As the polymerization time increases, the oxidation–reduction potentials of PDMA of all acids shift to being more positive and negative, due to the greater diffusion times of the counter ion for the redox reaction through the thicker films. Chui *et al* (1992) studied the effect of polypyrrole film thickness on cyclic voltammograms. The current–potential curve expanded and the potential difference ($\Delta E_p = E_{pa} - E_{pc}$) increased with the increase in film thickness as the amount of dopant increased. However, they obstructed further anions permeation, thus, higher potential was required for anion movement on the film.

On the other hand, Elmansouri *et al* (2007, 2009) showed that the oxidation potentials and currents of different supporting electrolytes depended on the nature and size of the anion present in the solution. The oxidation current was proportional to the speed of the electropolymerization reaction, this suggested faster growth kinetics. The oxidation current increased with increase in film thickness, as a function of the growth kinetics (Elmansouri *et al* 2007, 2009).

Figure 5. Effect of H_2SO_4 concentration on response time at 3·5 V of PDMA coated electrochemically polymerized ITO.

4. Conclusions

The synthesized PDMA films show reversible colour change from yellow to green representing the transition between the leucoemeraldine (reduced) state and emeraldine (oxidized) state which depend on the switching potentials. The PDMA/ITO electrochemically polymerized samples have mostly the same structural properties; the only difference is that the FT–IR bands show different counter ions of the oxalate and nitrate groups acting as counter ions with the protonated amine. The important differences of the PDMA synthesized in various acids at the same polymerization time are morphology and thickness of PDMA films, both factors lead to variations in the response time and the optical contrast. The increase of applied potential (1–3·5 V) and the H_2SO_4 electrolyte concentration (10^{-6}–10^{-1} M) contributed significantly to the decrease in the response time. With the increase of the polymerization time, the cyclic voltammetry showed a shift of the oxidation–reduction potentials of PDMA from all acids to being more positive and negative due to the greater diffusion time of the counter ion for the redox reaction through the thicker films.

Acknowledgements

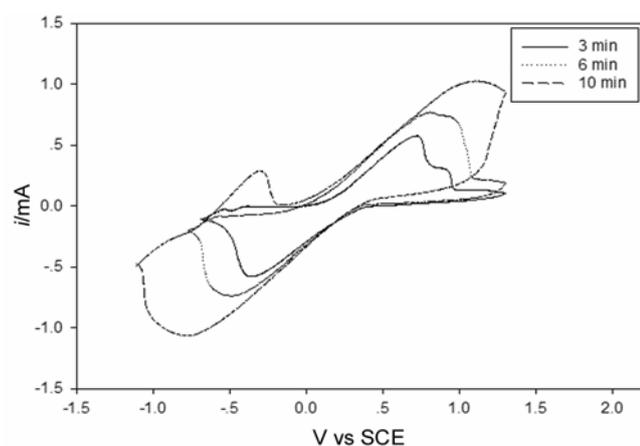**Figure 6.** Cyclic voltammograms of $H_2C_2O_4$–PDMA film at 3, 6 and 10 min deposition times within the potential range of –1 to 1·5 V; a scan rate of 10 mV/s and a 0·01 M of H_2SO_4 electrolyte solution background.

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