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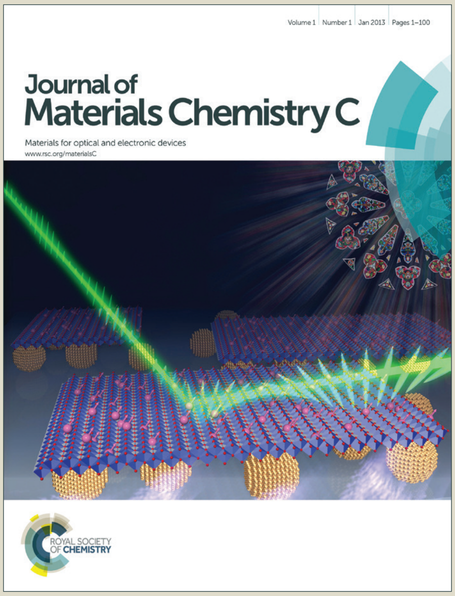

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ARTICLE

Solid-state electrochromic devices: relationship of contrast as a function of device preparation parameters

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The establishment of a relationship between device performance such as switch speed and photopic contrast with device composition, electrochromic polymer thickness, and gel electrolyte composition is reported here for a versatile one-step preparation method of relatively large area, 105 cm^2, solid-state electrochromic devices. Electrochromic polymer, hereby, generated from monomer after device construction, i.e. *in situ*, is a way to simplify the fabrication of electrochromic devices by reducing waste generation and assembly time as well as increasing the versatility of device manufacturing in open atmosphere. Photopic contrast is a critical property for electrochromic displays, windows, and lenses necessitating the study of how changing selected material and device properties such as monomer diffusion, thickness of the electrochromic polymer layer, and ionic conductivity of the electrolyte impacts electrochromic device functionality. More specifically photopic contrast performance is evaluated as a function of polymerization time, effective electrochromic polymer layer thickness, monomer loading, salt loading, thickness of gel electrolyte, and *in situ* conversion temperature. Photopic contrasts of 47% for poly biphenylmethyloxymethyl-3,4-propylenedioxythiophene (BPMOM-ProDOT), 46% for poly 2,2-dimethyl-3,4-propylenedioxythiophene (PProDOT-Me$_2$), and 40% for poly(3,4-ethylenedioxythiophene) (PEDOT) without background correction were achieved.

Introduction

Electrochromic materials can reversibly change from one colored state to another upon supplying a suitable charge and can be classified into three categories; inorganic materials, small organic molecules, and conductive polymers[1]. Among the different classes of electrochromic materials, conjugated polymers are of continued interest due to reported sub-second switch speeds, offerings of color variety, and high optical contrast[1,2] making them potential candidates for affordable displays, smart windows, eyewear, and color controlled textile.[1, 3-11]

At present, electrochromics consisting of conjugated polymers have not been commercialized yet possibly due to factors such as manufacturability, stability, color intensity, and contrast. Electrochromic devices can be prepared by electrodeposition of the electrochromic polymer onto tin-doped indium oxide (ITO) coated substrates from an electrolyte bath, and then assembled by a "sandwich" method.[12-14] For this purpose, rigorously cleaned dust and defect free ITO substrates are required. In earlier reports, electrochromic devices could be made in a one step method by converting the electroactive monomer to

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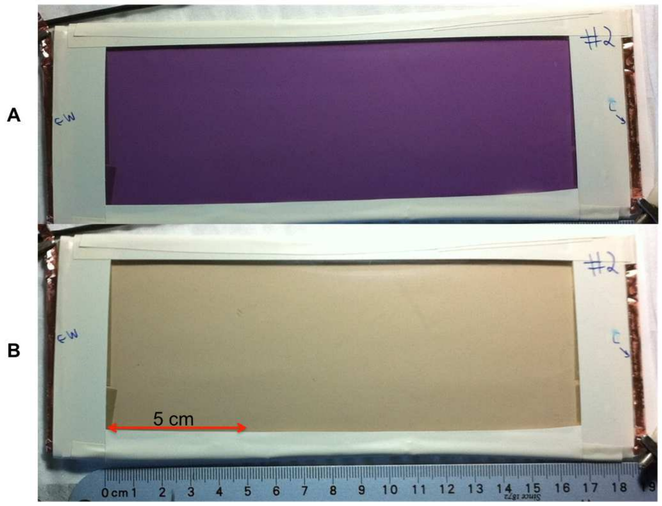

Fig. 1 (A) Colored state and (B) Bleached state for an electrochromic window of 105cm^2 active area using the *in situ* procedure with 2.5 wt% ProDOT-Me$_2$ in the electrolyte gel.

polymer, electrochemically, within the assembled solid-state device.[15] With this *in situ* process, the solid matrix is formed by the photopolymerization of an acrylate functionalized low molecular weight poly(ethylene glycol) (PEG) in the presence of a photoinitiator, salt, plasticizer, and monomer. The electrochromic polymer forms within the solid matrix upon application of an appropriate potential to polymerize the monomer. A requirement for this method is that the monomer-electrolyte solution should not be colored in order to achieve optimal photopic contrast. We have previously reported that electrochromic windows made from this *in situ* method have a higher contrast than those made from the corresponding conventional *ex situ* electrochemical polymerization approach due to a more transparent bleached state attributed to a lower absorption in the IR region imparted by increased inter-chain distances as previously described by Reynold's *et al.* using their solubilized, processable polythiophenes.[16] Another advantage of the *in situ* process is that complex patterns can be rapidly formed with relatively high-resolution large area substrates.[16] Recently in the literature, a high-throughput screening method was developed for rapid color selection for electrochromic devices using the *in situ* method.[17]

Photopic contrast, optical memory, color uniformity, and switching speed are essential requirements for electrochromic devices. Contrast can be defined as the change in the transmittance between the two extreme redox states of the electrochromic polymer. The transmittance value is related to the charge density and the thickness of the conductive polymer layer.[18,19] Lim *et al.* have reported that the intensity of the color change for each redox state is both a device characteristic and a material characteristic.[20] For the *in situ* approach, as the conductive polymers are forming inside the solid matrix the thickness of the electrochromic polymer, ionic conductivity of the gel electrolyte, concentration of the monomer, distance between two electrodes, and the mobility of the ions have to be considered in order to achieve maximum contrast. In this study, the variables changed to understand the relationship between ionic conductivity and contrast were the concentrations of lithium trifluoromethanesulfonate (LITRIF), ionic liquid, and 1-butyl-3-methylimidazolium hexafluorophosphate. Also, the concentration of the monomer will affect the polymerization rate, which was varied for each monomer studied. Three different thiophene based monomers 3,4-ethylenedioxythiophene (EDOT), 2,2-dimethyl-3,4-propylenedioxythiophene (PProDOT-Me$_2$), Biphenylmethyloxymethyl ProDOT (BPMOM-ProDOT) were used wherein the highest contrast of 48% was achieved using PBPMOM-ProDOT without background correction. This value is higher than previously reported using the traditional *ex situ* electrodeposition method[15] (Fig. S1). According to the Stokes-Einstein equation, the rate of monomer diffusion is temperature dependent. To evaluate the effect of temperature on the assembled device during electropolymerization, the temperature was varied from 22 °C to 35 °C. Herein, after introducing all the optimized parameters on a relatively large area, 105cm^2, optical defect free electrochromic devices have been fabricated using the *in situ* method. These devices were fully characterized for switching speed and photopic contrast using absorptiometry and chronocoulometry.

Experimental

Materials

Propylene carbonate (PC), poly(ethylene glycol) diacrylate (M$_n$ = 700) (PEG-DA), Lithium trifluoromethanesulfonate (LITRIF), 2,2-dimethoxy-2-phenyl-acetophenone (DMPAP) and 1-butyl-3-methylimidazolium hexafluorophosphate were purchased from Sigma Aldrich and used as received. Indium doped tin oxide (ITO) coated glass (resistance 8-12 Ohm/sq) and polyethylene terephthalate (PET) were purchased from Delta Tech Inc and Bay View Inc, respectively.

Norland UV curable glue UVS-91 was purchased from Products Inc. ProDOT-Me$_2$ and BPMOM-ProDOT were synthesized according to reported procedures.[21-23] EDOT was purchased from Heraeus Clevios GmbH and vacuum distilled before use.

Instrumentation

The electrochemical studies were carried out using CHI 720c and 400a potentiostats. A Varian Cary 5000i UV-Vis-NIR was used for all optics studies. A UVP CL-1000 was used for UV curing.

Electrochromic Device Fabrication

The electrolyte solution was prepared according to the reported procedure.[24,25] Different weight percentages of various monomers were added to the electrolyte gel as specified in the

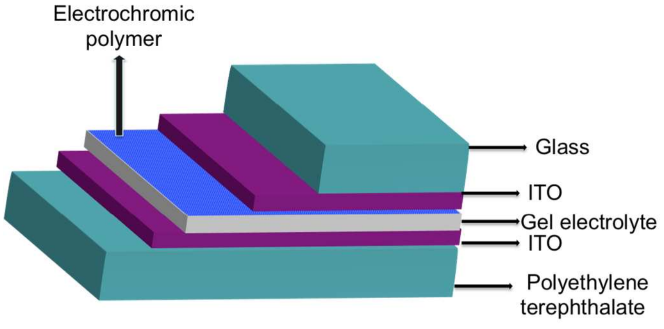

Fig. 2 Schematic diagram of the *in situ* electrochromic device.

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result and discussion section. The gel electrolyte (with monomer) was then drop cast between two ITO coated substrates. The thickness of the gel was controlled by using copper tape and a rubber gasket. The electrochromic device was cured by UV irradiation at 365nm (5.8mW/cm^2) for 5 minutes to provide a solid matrix, and UV curable glue was used to seal the device. 4 cm^2 active area electrochromic devices (Fig. S2) were used to optimize each parameter. Once optimized, devices with 105 cm^2 active area were made to demonstrate that these features could be translated to goggle-sized devices for real-world applications (Fig. 1). To reduce the iris effect for large area devices, adhesive copper tape was used around the entire perimeter of both ITO substrates.

Electrochemical polymerization

For electrochemical polymerization of alkylenedioxythiophene monomers inside the solid state assembled device, ITO coated glass, and ITO coated PET were used as working and counter electrodes, respectively. The reference electrode of a typical three-electrode cell was shorted with the counter electrode and a potential bias of 3V was applied to oxidize the electroactive monomers at the working electrode to form the electrochromic polymer. A ± 2V potential was applied to switch the device from the colored state to the bleached state. Thicknesses of the conductive polymer layers in the devices were calculated following the procedure of our previous work.[15] Although it is difficult to measure the true thickness of the polymer layer, as the electrochromic polymer grows inside the gel electrolyte matrix proximal to the working electrode, "effective" thicknesses were calculated. These calculations were performed with the assumption that the polymerization follows the Diaz mechanism and no side reaction has occurred.

Measurement of photopic contrast

Contrast is defined as the change in transmittance between the two extreme redox states of an electrochromic material. Often in literature, contrast is reported at a single-wavelength (λ_{max}). However, the best representation for reporting contrast is photopic contrast, which consists of a full-spectrum calculation because it's weighted to the sensitivity of the human eye.[26] For best accuracy, photopic contrast $\Delta T_{photopoic}$ is calculated using the transmittance values in the spectral range of 350-850 nm. For both bleached ($T_{photopic,b}$) and colored state($T_{photopic,c}$) in according to the following equation,

$$T_{photopic} = \frac{\int_{380}^{780} T(\lambda).S(\lambda).P(\lambda).d\lambda}{\int_{380}^{780} S(\lambda).P(\lambda)\, d\lambda}$$

and photopic contrast,

$$(\Delta T_{photopoic}) = \%T_{photopic,b} - \%T_{photopic,c}$$

where P(λ) is the normalized spectral response of the human eye, S(λ) is the normalized spectral emittance of a blackbody (at 6000°K), and T(λ) is the spectral transmittance of the device.[26]
After formation of the electrochromic polymer inside the solid gel matrix, the device was switched for 5 cycles before acquiring a spectrum for each of the two extreme redox states. All spectra were performed without background correction. Average photopic contrast for each data point has an error bar that is within ± 1% T.

Switching speed

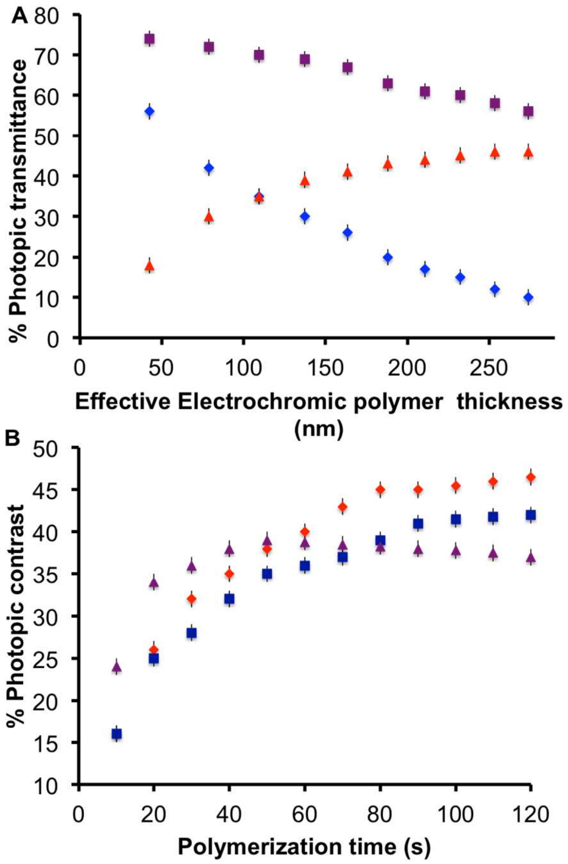

Fig. 3 (A) Photopic transmittance for colored state (blue diamonds), bleached state (dark purple squares) and respective contrast (red triangles) as a function of effective conductive polymer layer thickness for 2.5 wt% PProDOT-Me$_2$, (B) Photopic contrast of PEDOT, (dark purple triangle), PProDOT-Me$_2$ (blue square) and PBPMOM-ProDOT (red diamond) as a function of polymerization time for 0.07 mM concentrated monomer in gel electrolyte.

The transmittance value at the maximum absorbance wavelength (λ_{max}) was monitored as a function of time using a UV-Vis-NIR and a CHI720c potentiostat was used for potentiometric control.

Results and Discussion

Photopic contrast as a function of polymer layer thickness

Generally, the film thickness for a conjugated polymer prepared by electrochemical polymerization is directly proportional to the charge density that passes during electrochemical polymerization.[18] This has been established for conventional electrochemical polymerization from oxidation of the monomer in the bulk solution onto various electrodes, as well as having been previously reported for the *in situ* electrochemical polymerization of the monomer within a gel electrolyte near the surface of the optically transparent electrode. The transmittance of an anodically coloring electrochromic polymer in both the bleached and colored states corresponding to the oxidized and neutral states, respectively, is proportional to thickness in accordance to Beer's law. Previously reported for the *in situ* preparation of electrochromic polymers within a gel electrolyte, a method for calculating an effective conjugated polymer thickness was contrived.[15] Fig. 3(A) shows the percent photopic

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Table 1 Effect of gel electrolyte thickness on photopic contrast of PProDOT-Me_2.

Thickness of gel electrolyte (mm)	Charge consumed (C/cm^2)	PProDOT-Me_2 thickness (nm)	% Photopic contrast
0.34	$1.83 X 10^{-2}$	175 ± 5	45.5 ± 1 %
0.54	$1.50 X 10^{-2}$	140 ± 5	39.5 ± 1 %
1.19	$1.41 X 10^{-2}$	135 ± 5	37 ± 1 %
2.54	$8.60 X 10^{-2}$	132 ± 5	34.5 ± 1 %

transmittance (%$T_{photopic}$) of the bleached and colored states of an electrochromic device as a function of the effective electrochromic conjugated polymer thickness wherein the conjugated polymer is PProDOT-Me_2 prepared from a gel electrolyte solution containing 2.5 wt% of monomer, ProDOT-Me_2. Further, Fig. 3(A) shows the photopic contrast of the electrochromic device as a function of effective PProDOT-Me_2 thickness. The %$T_{photopic}$ of the colored and bleached states decrease upon increasing effective PProDOT-Me_2 thickness, and photopic contrast saturates at 46% at *ca.* 200 nm. The general trend of Fig. 3(A) is also observed for the other two electrochromic polymers studied, PEDOT and PBPMOM-ProDOT with the difference being the polymerization time to achieve an effective polymer film thickness at photopic contrast saturation, and the photopic contrast saturation value achieved. Time to achieve polymerization to give the effective polymer thickness at saturation of photopic contrast is dependent upon the monomer diffusion rate, and the concentration of the monomer in the electrolyte gel. Diffusion values for EDOT, ProDOT-Me_2, and BPMOM-ProDOT within this specific gel matrix at 0.07M loadings are reported to be $8.6X10^{-11}$ m^2/s, $1.11X10^{-12}$ m^2/s, and $3.89X10^{-13}$ m^2/s, respectively. Generally, the diffusion coefficients would fit the order that $D_{EDOT} > D_{ProDOT\text{-}Me2} > D_{BPMOM\text{-}ProDOT}$. Therefore, the polymerization of EDOT to produce an effective polymer film thickness at photopic saturation is expected to happen on a shorter time scale than that of ProDOT-Me_2 and BPMOM-ProDOT. Fig. 3(B) shows the relationship between photopic contrast vs polymerization time for each of the three different monomers using 0.07M of the monomer in the gel electrolyte. Among these three polymers, maximum photopic contrast was obtained for PBPMOM-ProDOT due to the high photopic transmissivity of the clear state. %$T_{photopic}$ for PBPMOM-ProDOT is 60% which is 5% and 2% higher than that of PEDOT and PProDOT-Me_2, respectively. The general enhancement of bleached state transmissivity has been explained by Reynolds *et al.*[16] in earlier reports and is related to an increase in distance between conjugated polymer chains which translates to a reduced absorbance in the near infrared. A lower absorbance in the near infrared means a lower absorption tail for this transition in the visible region translating to a higher bleach state transmissivity.

Photopic contrast as a function of Monomer loading

According to the Cottrell equation, charge consumption is directly related to the diffusion coefficient of the electroactive species. By changing the concentration of the monomers the rate of diffusion of the electroactive species towards the working electrode will vary and a different amount of charge will be consumed during polymerization. This results in a different transmittance value of each redox state, and as a result the contrast of the device will be different. The rate of diffusion is related to the concentration of the monomer in the gel electrolyte.[17] Photopic contrast of electrochromic devices with concentrations of 1, 2, 2.5, 3 and 5 wt% ProDOT-Me_2 were measured as a function of polymerization time and these results are shown in Fig. 4. The maximum photopic contrast for a conjugated polymer prepared from the ProDOT-Me_2 monomer at a concentration of 1 wt% is 41 ± 1 %T while 2, 2.5, and 3 wt% monomer loaded devices achieved maximum photopic contrasts of 43 ± 1, 46 ± 1, and 43.5 ± 1 %T, respectively. At the concentration of 5 wt% monomer initially had a value of (40 ± 1) % photopic contrast at a shorter conversion time of 30s as compared to the other four concentrations. By increasing the polymerization time the bleached state loses in transmittance are possibly due to the formation of more oligomers. Devices with a higher concentration of ProDOT-Me_2 were found to reach maximum contrast faster than those with a lower concentration.

Photopic contrast as a function of gel electrolyte thickness

To study the effect of solid gel electrolyte layer thickness with respect to photopic contrast of electrochromic devices, several devices were made having thicknesses ranging from 0.34 mm to 2.54 mm. According to the data listed in Table 1 at a concentration of 2.5 wt% ProDOT-Me_2, it is apparent that the thicker gel electrolyte consumed less charge compared to the

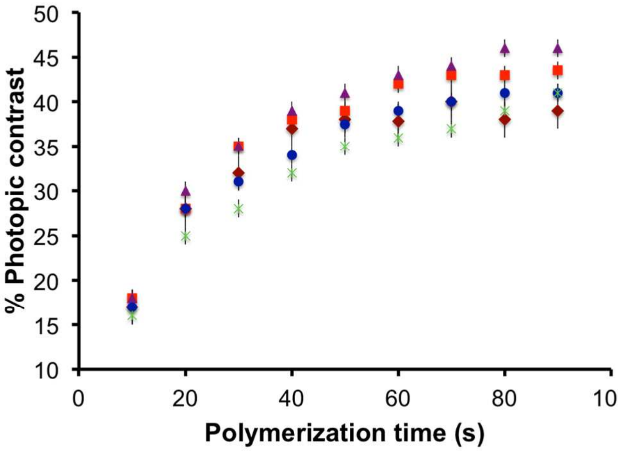

Fig. 4 Photopic contrast as a function of polymerization time for 1, 2, 2.5, 3 and 5 wt% ProDOT-Me_2 in gel electrolyte using the *in-situ* method (represented by purple square, red circle, blue triangle, green star, and dark red diamond respectively).

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Table 2 Redox switching speeds for maximum achievable photopic contrast.

EC polymer	$\%T_{photopic, b}$	$\%T_{photopic, c}$	Coloring(s)	Bleaching(s)
PEDOT	55%	16%	1.8	1.8
PProDOT-Me_2	58%	12%	1.8	3.5
PBPOM-ProDOT	60%	12%	1.8	3.2

thinner gel electrolyte for a given conversion time by increasing the distance between two electrodes. As a result, a thinner effective conductive polymer layer was formed which results in a lower photopic contrast. By increasing the polymerization time, more monomer will be converted and the desired effective polymer layer thickness can be achieved to obtain the maximum photopic contrast. For example, the electrochromic device with 2.54 mm thickness of gel electrolyte has a 10% lower photopic contrast than the maximum achievable contrast by increasing the conversion time.

Optimization of salt concentration

Upon increasing the salt concentration in a gel, the ionic conductivity will increase until a maximum is achieved. Upon further increase of salt concentration beyond this maximum, the ionic conductivity has been reported to drop due to issues such as aggregation of the salt and/or crystallization. Higher ionic conductivities contribute to a higher contrast since more mobile electrolyte leads to an increased doping level during polymerization, thus affecting polymer formation. As %T for both neutral and oxidized states decays exponentially by increasing the charge densities,[27] hence a maximum contrast is achieved. Increasing ionic conductivity will also increase the speed of an electrochromic polymer switching between the bleached and colored states, which in turn can lead to an observed change in photopic contrast based upon the fixed time that the contrast is observed. Different concentrations of LITRIF salt, 2.38 wt% to 13 wt% LITRIF were dissolved into 1:1 PC: PEG-DA and the conductivity was measured. The ionic conductivity doubled for 9 wt% salt (σ = 0.56 mS/cm^2) with respect to 2.4 wt% salt (σ = 0.28 mS/cm^2), due to an increase in number of ionic charge carriers while maintaining solubility in the gel matrix. Addition of more salt into the electrolyte causes the conductivity to decrease because of slower segmented motion of the polyelectrolyte chain due to ion aggregation.[28] Photopic contrast was measured as a function of salt loading using a constant concentration of 2.5 wt% of EDOT, for constant gel matrix thickness of 0.5 mm. Electrochromic devices prepared using 9 wt% salt achieved the highest photopic contrast 39% (55%T to 16%T).

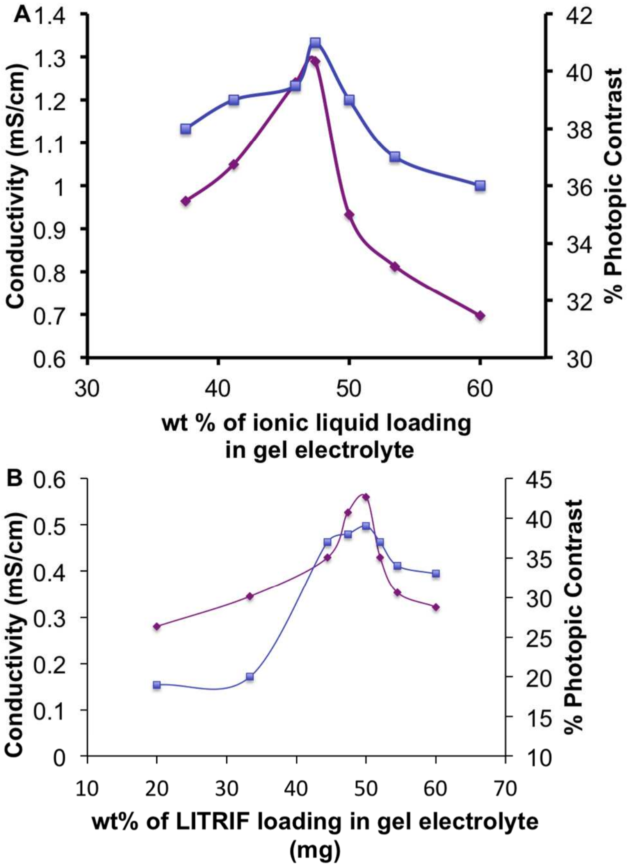

Fig. 5 (A) Plot of a PEDOT electrochromic device photopic contrast (dark purple diamonds) and ionic conductivity of solid gel electrolyte (blue squares) as a function of LITRIF (top) and ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (B) concentration.

The salt concentration study was also performed using an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (IL), and the same relationship was established between ionic conductivity and photopic contrast. Fig. 5 shows the plots for ionic conductivity and percent photopic contrast as a function of percent salt in the gel electrolyte for both the LITRIF and ionic liquid systems. The maximum ionic conductivity for the gel layer containing ionic liquid (σ = 1.29 mS/cm^2) is higher than that for the LITRIF system (σ = 0.56 mS/cm^2), and, as a result, the photopic contrast is higher by *ca.* 2%.

Switching speed of the *in situ* electrochromic devices

Transitioning or switching an electrochromic device from the bleached to colored state or vice versa is an electrochemical process involving electron transfer between the electrochromic polymer and the electrode coupled with the diffusion of charge compensating ions. Considering that the electrochromic is a conjugated polymer, in the bleached state it is electrically conductive, whereas in the colored state, it is an electrical insulator. Generally, reported switching speed is the time required for 95% of the transmittance change to take place at λ_{max} from one state to the other.[29] In order to determine the switching speed, %T was monitored during application of a square wave potential. Devices were subjected to +2 to -2V and the transmittance value recorded at the λ_{max} by a spectrophotometer.

The time required to switch the thicker PProDOT-Me_2 film (>160 nm) was higher than thinner films, 1.8 s to obtain the colored state (26 ± 1) %T to (67 ± 1%) %T while bleaching

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Table 3 Temperature study for electrochromic polymer preparation using 2.5 wt% ProDOT-Me_2 in gel-electrolyte with a constant polymerization time of 20s.

T (°C)	$\%T_{photopic, b}$	$\%T_{photopic, c}$	% Photopic contrast
22	73	44	29
25	73	37	36
28	69	32	37
30	67	28	39
35	67	27	40

takes 3.5 s. Thinner films (<100 nm) switch faster with times of 1.5 s from (35 ± 1) %T to (70 ± 1) %T for the same EC devices. Table 2 shows the switching speeds for maximum achievable photopic contrast of different electrochromic polymers using *in situ* method. For three different EC systems the switching speed for bleaching is different while the coloring speed is almost the same, 1.8 s to achieve the maximum contrast. For the bleaching process PEDOT switches faster than PProDOT-Me_2 and PBPMOM-ProDOT. As the polymer structures are more compact in the neutral state compared to the oxidized state more time is required for bleaching to undergo the conformational relaxation than the coloring process.[30-31] The switching speed also changes with the viscosity of the system. For the more viscous ionic liquid system the switching speed is 4.2 s for PEDOT bleaching whereas it takes only 1.8 s to fully bleach the LITRIF system.

Effect of temperature during polymerization

The photopic contrast for electrochromic polymers prepared from ProDOT-Me_2 with a polymerization time of 20 seconds at 23°C, 25°C, 28°C, 30°C and 35°C is shown in Table 3 (with the concentration of ProDOT-Me_2 at 2.5 wt% and the gel electrolyte layer thickness at 0.55 mm). Photopic contrast data was obtained for these devices at room temperature, approximately 25°C. High contrast devices were obtained upon raising the temperature of the gel during device preparation since the diffusion rate of the monomer as well as the rate of polymerization increased. Thereby allowing for a thicker conductive polymer layer formation for the same polymerization time. Temperature experiments were also carried out to activate devices using longer conversion times, yet the maximum contrast achieved remained to be 46% for PProDOT-Me_2. Temperature serves as only an optimization in the time it would take to make a device of a given contrast, not as a means to increase the contrast value beyond that obtained by changing the other variables studied here.

Conclusions

As the electrochromic polymer is formed inside the solid gel matrix with the *in situ* approach, both material and device characteristics have bearing on the optical properties of the electrochromic devices. Some important factors such as thickness of the electrochromic polymer, polymerization time, diffusion coefficient of the electroactive species, thickness of the gel electrolyte, ionic conductivity of the solid matrix and the temperature of the system are studied and established a relationship with photopic contrast. By optimizing the above mentioned parameters a large defect free electrochromic window of 105 cm^2 active area was successfully made using the one step *in situ* approach. This method could reduce cost and waste as well, and can also be used to fabricate large area devices.

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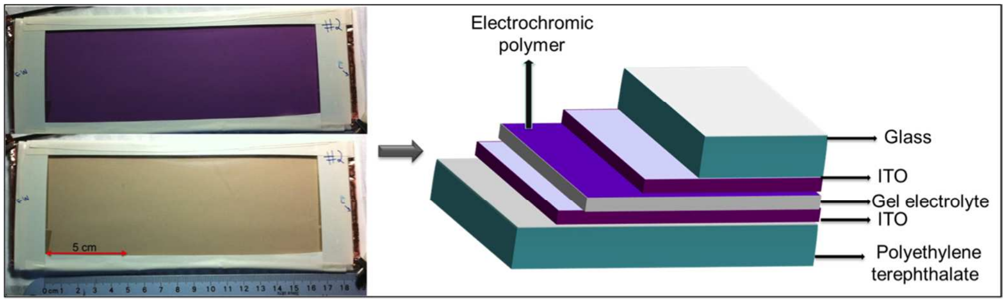

The establishment of a relationship between device performance parameters is reported here for a versatile one-step preparation method of a large area solid-state electrochromic device.
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