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

Amrita Kumar, Michael T. Otley, Fahad Alhasmi Alamar, Yumin Zhu, Blaise G. Arden and Gregory Sotzing*

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 cm², 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-Me₂), 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. 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 making them potential candidates for affordable displays, smart windows, eyewear, and color controlled textile. 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. 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
between two electrodes, and the mobility of the ions have to be
polymer, electrochemically, within the assembled solid-state
electrolyte gel. Also, the

device.

thickness of the electrochromic polymer, ionic conductivity of
the variables changed to understand the relationship between
considered in order to achieve maximum contrast. In this study,
the gel electrolyte, concentration of the monomer, distance
conductive polymers are forming inside the solid matrix the
lithium trifluoromethanesulfonate (LITRIF), ionic liquid, and 10
ionic conductivity and contrast were the concentrations of
electrochromic polymer forms within the solid matrix upon
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.8,19 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

different thiophene based monomers 3,4-
ethyleneedioxythiophene (EDOT), 2,2-dimethyl-3,4-
propylenedioxythiophene (PProDOT-Me$_2$), Biphenylmethyloxymethyldi
ProDOT (BPMOM-ProDOT) were used wherein the highest contrast of 48% was achieved using
PBMOM-ProDOT without background correction. This value
is higher than previously reported using the traditional ex situ
electrodeposition method17 (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, 105 cm$^2$,
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

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

**Fig. 2** Schematic diagram of the in situ electrochromic device.
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/cm²) for 5 minutes to provide a solid matrix, and UV curable glue was used to seal the device. 4 cm² active area electrochromic devices (Fig. S2) were used to optimize each parameter. Once optimized, devices with 105 cm² 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. 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 (\(\lambda_{\text{max}}\)). 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. For best accuracy, photopic contrast \(\Delta T_{\text{photopic}}\) is calculated using the transmittance values in the spectral range of 350-850 nm. For both bleached (\(T_{\text{photopic,b}}\)) and colored state(\(T_{\text{photopic,c}}\)) in accordance to the following equation,

\[
T_{\text{photopic}} = \int_{350}^{850} T(\lambda) \frac{S(\lambda) \cdot P(\lambda) \cdot d\lambda}{S(\lambda) \cdot P(\lambda) \cdot d\lambda}
\]

and photopic contrast,

\[
(\Delta T_{\text{photopic}}) = \%T_{\text{photopic,b}} - \%T_{\text{photopic,c}}
\]

where \(P(\lambda)\) is the normalized spectral response of the human eye, \(S(\lambda)\) is the normalized spectral emittance of a blackbody (at 6000°K), and \(T(\lambda)\) is the spectral transmittance of the device. 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

The transmittance value at the maximum absorbance wavelength (\(\lambda_{\text{max}}\)) 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. 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 \(\textit{in situ}\) 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 \(\textit{in situ}\) preparation of electrochromic polymers within a gel electrolyte, a method for calculating an effective conjugated polymer thickness was contrived. Fig. 3(A) shows the percent photopic
transmittance ($\%T_{\text{photopic}}$) 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 $\%T_{\text{photopic}}$ 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 EDOM, ProDOT-Me$_2$, and BPMOM-ProDOT within this specific gel matrix at 0.07M loadings are reported to be $8.6 \times 10^{-12}$ m$^2$/s, $1.11 \times 10^{-12}$ m$^2$/s, and $3.89 \times 10^{-13}$ m$^2$/s, respectively. Generally, the diffusion coefficients would fit the order that $D_{\text{EDOT}} > D_{\text{ProDOT-Me}} > D_{\text{BPMOM-ProDOT}}$. Therefore, the polymerization of EDOM 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. $\%T_{\text{photopic}}$ 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. 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 bleached 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. 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

<table>
<thead>
<tr>
<th>Thickness of gel electrolyte (mm)</th>
<th>Charge consumed (C/cm$^2$)</th>
<th>PProDOT-Me thickness (nm)</th>
<th>% Photopic contrast</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>$1.83 \times 10^{-2}$</td>
<td>175 ± 5</td>
<td>45.5 ± 1 %</td>
</tr>
<tr>
<td>0.54</td>
<td>$1.50 \times 10^{-2}$</td>
<td>140 ± 5</td>
<td>39.5 ± 1 %</td>
</tr>
<tr>
<td>1.19</td>
<td>$1.41 \times 10^{-2}$</td>
<td>135 ± 5</td>
<td>37 ± 1 %</td>
</tr>
<tr>
<td>2.54</td>
<td>$8.60 \times 10^{-2}$</td>
<td>132 ± 5</td>
<td>34.5 ± 1 %</td>
</tr>
</tbody>
</table>

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).
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 effective conductive polymer layer was formed which results in 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, 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: PEG0DA and the conductivity was measured. The ionic conductivity doubled for 9 wt% salt (σ = 0.56 mS/cm) with respect to 2.4 wt% salt (σ = 0.28 mS/cm), 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. 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). 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) is higher than that for the LITRIF system (σ = 0.56 mS/cm), 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 insulating, 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 λmax from one state to the other. 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 λmax by a spectrophotometer. The time required to switch the thicker PProDOT-Me2 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.
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-Me2 and PBPOMOM-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.\textsuperscript{30} The switching speed also changes with the viscosity of the system. For the more viscous 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-Me2 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-Me2 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-Me2. 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.

### Acknowledgements

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### References

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.