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# Study of Electrochromic Properties of PEDOT:PSS for Tunable Filter Optics with Lithium Salt Electrolyte

**Nisakon Janthajam[1], Shu-Han Hsu[1,*], Sakoolkan Boonrung[2]**

[1]Sirindhorn Institute International of Technology, Thammasat University, Pathum Thani 12120, Thailand
[2]National Science and Technology Development Agency, National Electronics and Computer Technology Centre, Pathum Thani 12120, Thailand

* Corresponding author e-mail: shuhanhsu@siit.tu.ac.th

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**Abstract:** Nowadays, conductive polymers based on poly(3,4-ethylenedioxythiophene), poly(styrene sulfonic acid), or PEDOT:PSS, have been employed as a flexible and transparent coating in various significant electronic applications. With the demand for electrochromic properties, such as in electronic displays, further research into its electrooptic properties is required, especially the systematic understanding to obtain the optimized switching. Our research investigates the electrooptic properties of the PEDOT:PSS film, particularly the refractive index changing under various applied biases. The electrochromic device is prepared in a simple fashion, and the electroactive layer of PEDOT:PSS thickness is defined via spin-coating between two indium tin oxide (ITO) substrates. To increase the switching properties of PEDOT:PSS, lithium perchlorate ($LiClO_4$) was prepared in acetonitrile, as the electrolyte in varied concentrations of 1.195 M, 1.5 M, and 2.0 M, respectively. A potential voltage of -4.0 V to 0.0 V is utilized to study the device's electrochromic properties with the step 5 mV/s continuously. Finally, the optical properties are characterized using the spectroscopy method based on real-time measurement of the transmission spectrum and transmission matrix calculations. The change in visible light absorption, transmission, and film color is recorded under a switching cycle that shows consistent behavior. This allows the further utilization of such a hybrid structure for possible tunable filter applications.

**Keywords:** Electrochromic, PEDOT:PSS, Optical, Lithium salt, Electrolyte

## 1. Introduction

An electro-optic (EO) studies explores the merging of optical and electrical principles and investigates such applications to improve our quality of life. Furthermore, as an acoustic-optic modulator (AOM), it is an electrically controlled transmission to execute the differential refractive index [1]. A tunable optical filter (TOF) is one of the applications for creating a refractive index change [2]. A narrow pass-band filter allows wavelengths to propagate through the device. Many studies have been conducted to investigate the application of tunable techniques such as Fabry-Perot (FP) cavity structure, liquid crystal FP etalon, thin-film redox ability, and so on. Specifically for thin-film interference, a substrate surface is deposited to achieve a new refractive index by transferring its dielectric structure. Electrical actives have been demonstrated on electrode substrates with working electrodes, such as electrochromic

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(EC) materials [3]. Many materials have been searched to greatly improve device design based on optical phenomena such as Fabry-Perot interference (FPI).

Okutan and co-workers proposed a poly(3,4-ethylenedioxythiophene), poly(styrene sulfonic acid), or PEDOT:PSS, with varying types of electrolyte-treated PEDOT:PSS and characterized current versus time detection, and demonstrated transmittance along visible wavelengths from 30-90 nm [4]. As a result, the transmittance of PEDOT:PSS appears to be 70% after applying with $LiClO_4$ 70% when bleached, which is greater than the initial hue of PEDOT:PSS. The repeated current overtime measurement reveals the charge carrier presented in the device. However, the responses depend on factors such as thickness, potential voltage scan rate, and electrolyte materials. In contrast, Zhu et al. conducted a research on PEDOT:PSS conductivity using a variety of lithium salts ($LiClO_4$) when compared to the other lithium salts showing the highest conductivity exceeding 500 σ ($S{\cdot}cm^{-1}$) at $Li^+$ ion with 30% concentration [5]. Anderson et al. proposed a method for fabricating EC devices using flexible materials [6]. They studied the pristine PEDOT:PSS layer and mixed PEDOT:PSS with $LiClO_4$ for the electrochromic effect of the film. As a result, the mixture of PEDOT:PSS with $LiClO_4$ shows a higher significant transmission change of 41% at wavelength 640 nm. Their report mentioned that the conductivity of the mixture was lower than the pristine PEDOT:PSS layer.

Okutan et al. studied the device prepared by layer-by-layer deposition of PEDOT:PSS on polyethylene terephthalate film (PET) substrate [4]. The device has 10 bilayers of PEI polymer and electrochromic material (PEDOT:PSS) and uses an electrolyte in solution form. However, our work implemented the single layer of the pristine PEDOT:PSS with lithium perchlorate electrolyte gel. Our study focuses on the electroactive device fabrication with a thinner electrochromic layer (PEDOT:PSS) around 300 nm in a simple preparation method. The electrochromic material of PEDOT:PSS was spin-coated on an ITO glass substrate with a spin speed of 1250 rpm. Thus, the film can be prepared with a thinner thickness than Okutan's work. Also, a gel form of electrolyte was used for more practical utilization with less concern of electrolyte leaking and concentration change due to solution evaporation. Therefore, electrolyte concentrations of 1.195 M, 1.5 M, and 2.0 M were used to optimize the electrochromic effect for a single layer of PEDOT:PSS film.

## 2. Methodology

### 2.1 Experimental

A substrate was prepared by sonicating an indium tine oxide (ITO) glass slide in isopropanol (IPA), and in deionized water for 10 minutes. An ITO glass slide was subsequently dried with nitrogen. Before coating the ITO with PEDOT:PSS solutions, $O_2$-plasma was used to activate the ITO for 5 minutes. Pristine PEDOT:PSS (14-15%wt in water) was spin-coated on ITO with 1250 rpm for 30 seconds and the substrate was dried at temperatures 60 °C for 5 minutes on a hotplate. A hole of 1 cm in radius was created in the middle of 3 mm thick Polydimethylsiloxane (PDMS). This stamp was placed onto the PEDOT:PSS film. Finally, the electrolyte solution was dropped into the hole area and closed by placing another ITO substrate, as demonstrated in Figure 1. Electrolyte was prepared by dissolving a $LiClO_4$ in acetonitrile (ACN) and adding 100 mg of polyethylene oxide (PEO). This will create a gel-like electrolyte that provides a certain viscosity to avoid leaking during the device's operation. The concentration of electrolyte was varied as 1.195 M, 1.5 M, and 2.0 M.

### 2.2 Characterization

An optical system collects the transmission spectra of an electrochromic device. The system is composed of a halogen light source (HL-2000, Ocean Insight) illuminating from top to bottom, a device holder placed in the middle section, and the spectrometer (Thorlabs CCS100/M, range 200-1000 nm) located at the bottom, as illustrated in Figure 2. The potential voltage applies through the cyclic voltammetry (Metrohm Autolab EV, type PGSTAT128N) with varying voltage from 0.5 V to -4.0 V and a scan rate of 0.005 V/s with step 0.05 V/s. This work mainly focuses on the electrochromic properties of PEDOT:PSS. Hence, the optical system detects the transmission. A potential voltage held at -4.0 V (initial) and 0.0 V for 120 s. In addition, the transmission records raw intensity from the spectrometer through Thorlabs OSA software every 15 s until the measurement finishes.

The electrochromic device successfully utilizes $LiClO_4$ electrolyte with the pristine PEDOT:PSS. The device contains an electrolyte gel ($LiClO_4$) coated on top of the PEDOT:PSS film surface that the electrolyte will allow ions to move freely. The PEDOT:PSS layer exhibits color changes in response to the applied electric bias with ionic insertion/ extraction mechanism. The assembly of the EC device is demonstrated in Figure 3. In this work, ITO is used as a transparent conducting oxide layer and PEDOT:PSS is an electrochromic layer, with $LiCl_4$ working as an electrolyte layer.

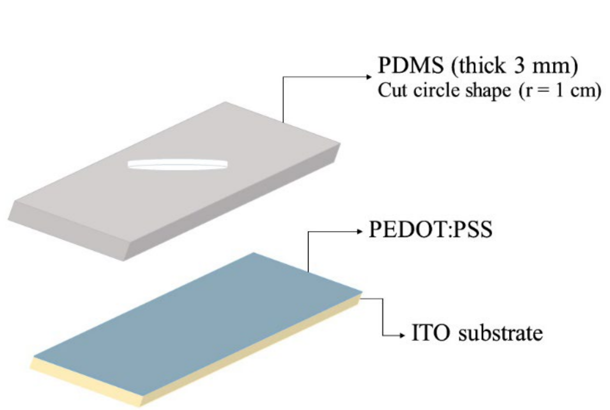



Figure 1 PEDOT:PSS device fabrication.

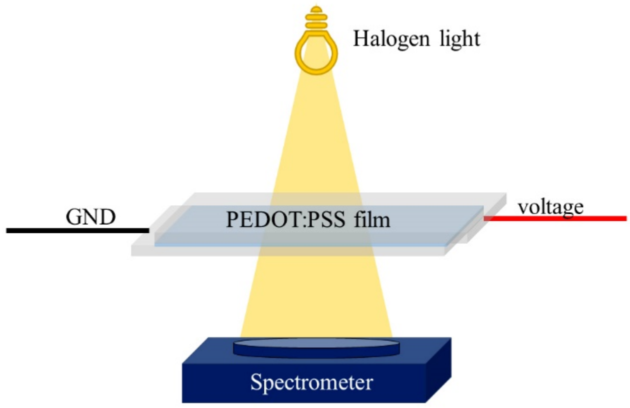



Figure 2 Schematic of optical system setup for electrochromic measurement.

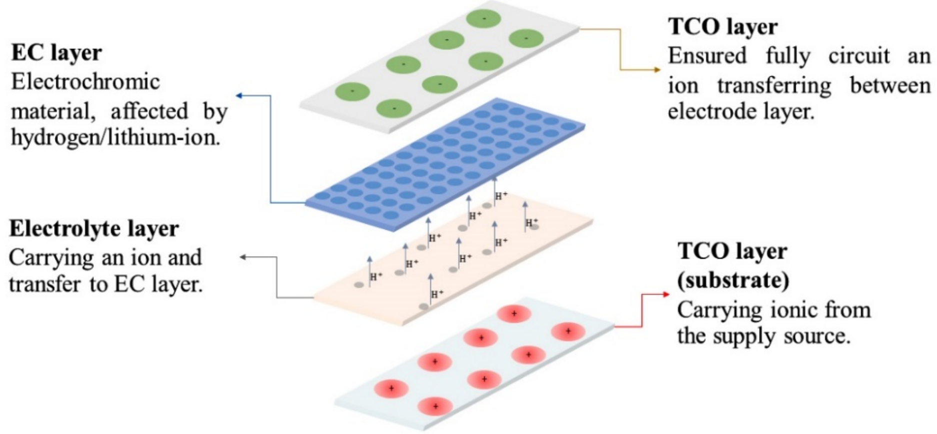
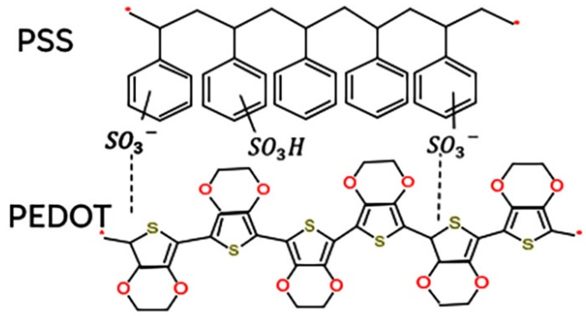



Figure 3 The electrochromic device overview of PEDOT:PSS, and the schematic mechanism of $LiClO_4$ electrolyte.

Equation (1) explains that $PEDOT^{n+}$ contributes to the positive charge while denoting the $PSS^{x-}$ as a negative charge. The reaction involves the transfer of n electrons from PEDOT:PSS in its negative state ($PEDOT:PSS^{x-}$). This process indicates a reduction reaction, where the polymer undergoes chemical modification through electron transfer.

$$\underset{\text{Light blue}}{(PEDOT)^{n+}(PSS)^{x-} + ne^-} \leftrightarrow \underset{\text{Dark blue}}{PEDOT:PSS^{x-}} \quad (1)$$

PEDOT:PSS structure is an essential conducting polymer consisting of positively charged PEDOT and negatively charged PSS, which contain sulfonate groups ($SO_3^-$). This blend forms a complex structure where PEDOT chains are intertwined with PSS chains. The negatively charged sulfonate groups of PSS interact with the positively charged PEDOT chains through electrostatic interactions, facilitating the formation of the complex. As a result, PEDOT:PSS exhibits enhanced electrical conductivity, improved film-forming properties, and increased stability.




Upon adding an electrolyte layer, a few steps are involved to reveal the switching behavior of electrochromic materials. The noticeable increase in ionic conductivity in the electrolyte is attributed to the simultaneous rise in ionic charge carrier concentrations of $Li^+$ ions as they diffuse through the finite PEO matrix. This is especially true in a layered structure where $Li^+$ ions and $H^+$ (PSS) are involved in redox reactions. Interestingly, $Li^+$ ions primarily participate in charge adjustment mechanisms within the core-shell architecture due to their higher mobility than $H^+$. In the final stage, there is a form of partial obstruction that results in accumulating a positive charge in a different layer known as $PEDOT^+$. Therefore, the charge separation was created across the PEDOT:PSS film [6,7].

## 3. Results and discussion

The electrochromic device was simply prepared using pristine PEDOT:PSS. No other substance was mixed. This work studies the switching effect of a gel electrolyte to obtain the optimized performance with a single layer of pristine PEDOT:PSS electrochromic material. Hence, the characterization of the film was focused on switching behavior using different electrolyte concentrations.

The section represents the results of three different $LiClO_4$ electrolyte solutions: 1.195 M, 1.5 M, and 2.0 M, respectively. Each concentration was applied over a single layer of pristine PEDOT:PSS coated on the ITO substrate. The potential bias was applied for switching monitoring. To optimize the current of the film, the voltage was set between 0.5 V to -4.0 V, and the scan rate was 5 mV/s.

Figure 4 illustrates a significant decrease in current from 0 μA to -25 μA as the electrolyte concentration rises to 1.195 M. However, at concentrations of 1.5 M and 2.0 M, the current remains notably low, at 0 μA and -0.25 μA, respectively. The observed attenuation in conductivity progression upon the incremental introduction of $LiClO_4$ salt into pure PEO can be elucidated by the intricate charge transport mechanism within PEO solid polymer complexes. This mechanism entails the dissociation of $Li^+$ cations from coordination oxygen at an adjacent site. The current behavior depends on the $Li^+$ transfer between the electrolyte and electronic layers. Three concentrations of gel electrolyte were utilized to understand the ion assisted switching behaviors of the devices. It shows that 1.195 M is the best concentration for the device, showing good electrochromic switching behavior. However, higher electrolyte concentrations do not appear to show a positive response. This may be due to the increasing viscosity of electrolyte gel for 1.5 M and 2.0 M concentrations, and it may require higher switching redox potential.

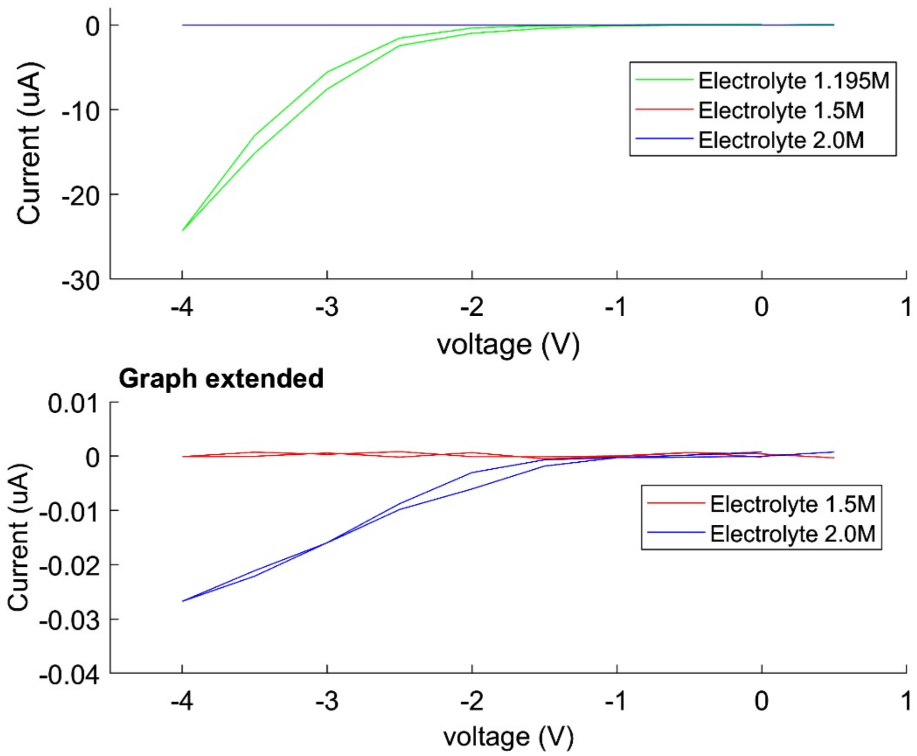



Figure 4 The current-voltage characterization of the electrochromic device with $LiClO_4$ electrolyte of 1.195 M (green), 1.5 M (red), and 2.0 M (blue) concentration, respectively.

In addition, the in-situ optical property was measured to represent the transmission property of the film that selected potential -4.0 V and 0.0 V of each concentration, shown in Figure 5. The device's transmission spectra were measured for the sample with 1.195 M, 1.5 M, and 2.0 M electrolyte concentrations at -4.0 V and 0.0 V applied voltage. Switching behavior can be observed for the device with a 1.195 M electrolyte concentration, showing around a 2% difference in transmission at 560 nm and a 4% difference in transmission at 920 nm (Figure 5(a)). However, for another two electrolyte concentrations of 1.5 M and 2.0 M, no clear switching can be observed (Figure 5(b) and 5(c)).

Figure 6 illustrates the photograph of the color-reversed state about Equation (1), the redox or reduction of PEDOT:PSS. This picture is the device with PEDOT:PSS film dropped by an electrolyte concentration of 1.195 M. In its initial state, it displays light blue without any potential voltage. The color becomes darker once the bias shoots at -4.0 V and then reverses to a brighter blue at 0.0 V.

The figure shows the transmission intensity change versus time at specific wavelengths of 560 nm and 920 nm. This is a continuous measurement made by consistently switching between -4.0 V and 0.0 V. This measurement provides information about the device's stability and reversibility. One can observe similar switching behavior at 920 nm between 36% and 32.5%, and a relatively smaller change at 560 nm, about 32% to 30% of the sample with electrolyte concentration of 1.195 M, for continuing five loop measurements (Figure 7(a)). However, for electrolyte concentration of 1.5 M, no change of transmission was observed with 37.5% at 560 nm and 51% at 920 nm (Figure 7(b)). For the device made with 2.0 M electrolyte, the transmission was slightly increased and then decreased when the third cycle of bias was applied, indicating that some ions may participate as a conductive path in the electrochromic polymer layer. However, the switching rate did not response to the applied voltage, accordingly (Figure 7(c)).

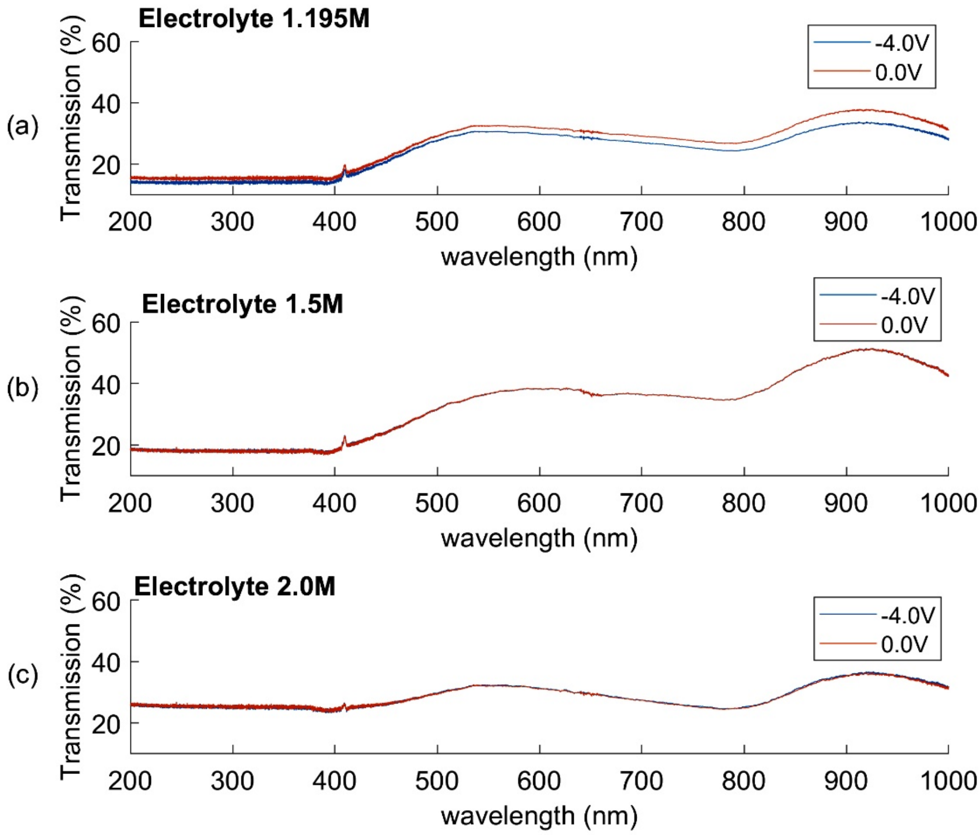



Figure 5 Transmission spectra of PEDOT:PSS/$LiClO_4$ films in three conditions, i.e., (a) 1.195 M, (b) 1.5 M, and (c) 2.0 M at initial -4.0 V and 0.0 V.

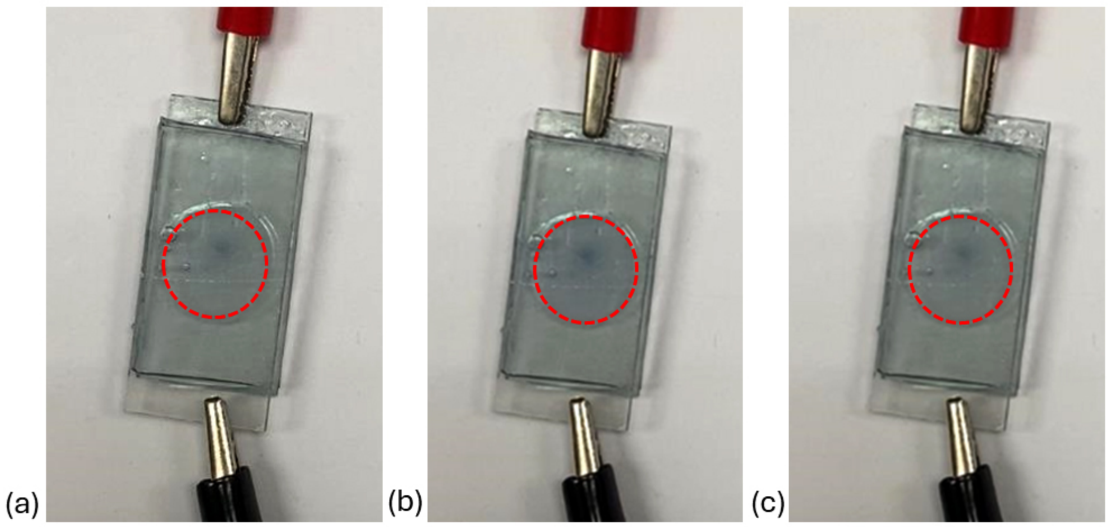



Figure 6 Photographs of PEDOT:PSS dropped an electrolyte 1.195 M; (a) Initial (without bias), and with applied voltage (b) -4.0 V and (c) 0.0 V.

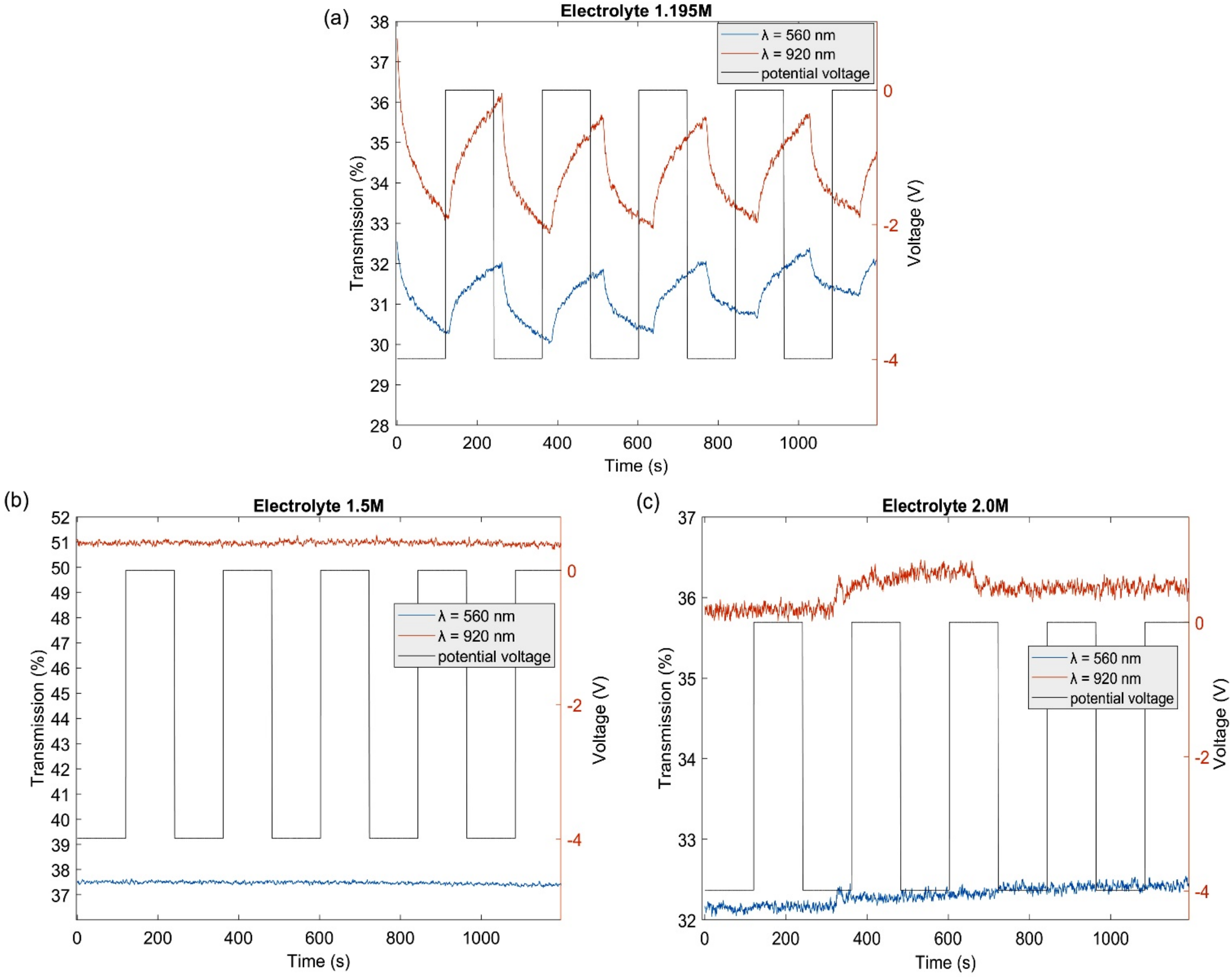



**Figure 7** Transmission intensity (raw data) versus time measurement at wavelengths 560 nm and 920 nm of the sample with electrolyte concentration of (a) 1.195 M, (b) 1.5 M, and (c) 2.0 M.

However, the lack of observable electrochromic changes in concentration 1.5 M and 2.0 cap M could be due to several combination factors, such as insufficient ion conductivity due to increasing viscosity in the electrolyte, inappropriately applied redox potential, or inadequate film preparation. This highlights the importance of optimizing electrolyte concentration for achieving desired electrochromic properties.

The noticeable increase in ionic conductivity in the electrolyte of 1.195 M is attributed to the simultaneous rise in ionic charge carrier concentrations. This is especially true in a layered structure where $Li^+$ ions and $H^+$ (PSS) are involved in redox reactions. Interestingly, $Li^+$ ions primarily participate in charge adjustment mechanisms within the core-shell architecture due to their higher mobility than $H^+$. In the final stage, there is a form of partial obstruction that results in accumulating a positive charge in a different layer known as $PEDOT^+$. The electronic configuration is altered under this charge separation. Therefore, the optical property of PEDOT:PSS has changed accordingly, which induces the color change of the film and its transmission property.

## 4. Conclusion

In conclusion, this study will fabricate and investigate the electrolyte in various concentrations to enhance its conductivity and improve PEDOT:PSS electrochromic properties. The results demonstrate that the concentration shows promising outcomes regarding color switching, stability, and reversibility. At a certain concentration, ensuring that ions move readily while maintaining film integrity over multiple switching cycles. There are stronger interactions between the electrolyte ions and the active components of the PEDOT:PSS film, leading to improved electrochromic performance in terms of response time and color contrast. As a result of Figure 7(a), only at this certain concentration does PEDOT:PSS show good performance in the electrochromic effect at a wavelength between 560 nm and 920 nm, the transmission drops. Besides, higher electrolyte concentrations do not achieve significant electrochromic effects. The experimental findings underscore the importance of optimizing electrolyte concentration to enhance the performance of electrochromic materials. Further research will be carried out to improve the switching by properly adjusting the PEDOT:PSS film thickness, electrolyte volume ratio, and operation bias to achieve better electrochromic behavior. This study contributes valuable insights into developing efficient electrochromic materials for diverse applications in optoelectronics and smart devices.

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## References

[1] J. F. Lotspeich, R. R. Stephens, D. M. Henderson, Electro-optic tunable filter, *Opt. Eng.* **20** (1981) 830-836.
[2] N. J. Goddard, A. E. Maturell, Tunable optical filter for colorimetric applications, *Appl. Opt.* **34** (1995) 7318-7320.
[3] A. Hein, C. Kortz, E. Oesterschulze, Tunable graduated filters based on electrochromic materials for spatial image control, *Sci. Rep.* **9** (2019) 15822.
[4] M. Okutan, D. Evecan, S. Yıldırım, E. Ö. Zayim, H. Deligöz, Investigating the effect of electrolyte types with various ionic liquids on the electrochromic performance of PEDOT:PSS based LbL multilayers, *Microelectron. Eng.* **234** (2020) 111454.
[5] Z. Zhu, H. Song, J. Xu, C. Liu, Q. Jiang, H. Shi, Significant conductivity enhancement of PEDOT:PSS films treated with lithium salt solutions, *J. Mater. Sci.: Mater. Electron.* **26** (2015) 429-434.
[6] A. E. X. Gavim, G. H. Santos, E. H. de Souza, P. C. Rodrigues, J. B. Floriano, R. C. Kamikawachi, J. F. de Deus, A. G. Macedo, Influence of electrolyte distribution in PEDOT:PSS based flexible electrochromic devices, *Chem. Phys. Lett.* **689** (2017) 212-218.
[7] J. Gurusiddappa, W. Madhur, R. P. Suvarna, K. P. Dasan, Studies on the morphology and conductivity of PEO/$LiClO_4$, *Mater. Today: Proc.* **3** (2016) 1454-1459.