JOURNAL of THE TURKISH CHEMICAL SOCIETY
SECTION: B
CHEMICAL ENGINEERING
TURKISH CHEMICAL SOCIETY

Effect of hBN on Response Times of PEO-Based Electrochromic Devices

Özge AKPINAR SARIHAN #[1,2], İbrahim İNANÇ #[1,2], Gediz UĞUZ#[3]

[1] University of Ondokuz Mayıs, Nanoscience and Nanotechnology Program, Samsun, Turkey.
[2] University of Ondokuz Mayıs, Metallurgy and Materials Engineering Department, Samsun, Turkey.
[3] University of Ondokuz Mayıs, Chemical Engineering Department, Samsun, Turkey.

Abstract: In this study, all solid state electrochromic devices (ECDs) without plasticizer such as propylene carbonate were fabricated by sol-gel spin coating method. WO_3 nanoparticles and PEO based polymer electrolyte solutions with hBN and without hBN nanoparticles were prepared. These solutions were sol-gel spin- and dip-coated on ITO-glass, respectively. For determining the effect of hBN nanoparticles, four configuration of ECDs were fabricated. The fast bleaching and coloring times of fabricated ECDs were obtained with hBN nanoparticles in WO_3 and PEO based polymer electrolyte thin films as 1.15 seconds. Glass/ITO/hBN-WO_3/hBN-PEO-based-polymer electrolyte/ITO/Glass electrochromic device is turned on and off 60 times. After 60 cycle, the device coloring time changed to 2-3 seconds, bleaching times changed to 30 seconds.

Keywords: Electrochromic devices, polymer electrolyte, sol-gel process, hBN nanoparticles.

Submitted: February 10, 2024. **Accepted:** March 22, 2024.

Cite this: Akpınar Sarıhan, Ö., İnanç, İ., & Uğuz, G. (2024). Effect of hBN on Response Times of PEO-Based Electrochromic Devices. Journal of the Turkish Chemical Society, Section B: Chemical Engineering, *7*(1), 69–76. https://doi.org/10.58692/jotcsb.1435022.

***Corresponding author. E-mail:** ozgeakpinar86@hotmail.com

1. INTRODUCTION

Optical transmittance of electrochromic devices (ECD) are arranged reversibly and persistently by applying a small voltage (Pehlivan et al., 2014) . An ECD has an ion conductive layer (electrolyte) is sandwiched between an electrochromic and ion storage layer. Electrochromic and ion storage are coated on transparent conductive electrodes. The device is protected by coating transparent conductive electrodes on plastic and glass surfaces. Ions are transferred between the ion storage and electrochromic layers through the electrolyte layer (Fu, 2010; Eren, 2018). The electroyte layer, small ions such as protons H^+ or lithium ions Li^+, rarely Na^+ and Ag^+, are used (Eren, 2018; Solovyev et al., 2016).

Solid electrolytes have properties such as not leaking, easy to prepare, and perform good adhesion to electrolytes (Jeong et al., 2021). Polymer electrolyte consists of polymers and salt. PEO or PEO-derived polymers dissolved lithium salts well that do not allow crystallization even at low temperatures. Despite the advantages, Solid polymer electrolytes have low room-temperature conductivity (Fullerton-Shirey et al., 2010).

Usually, both crystalline and amorphous phases are present in polymer electrolytes. Amorphous phases have higher conductivity than crystalline phases, and ionic conductivity increases by adding plasticizers to amorphous phases (Fu, 2010). Polymer electrolyte conductivity is increased by the addition of nanoparticle filler (Fullerton-Shirey et al., 2010). Additionally, device's performance is increased by adding nanoparticles to polymer electrolytes (Pehlivan et al., 2014).

Tang et al. (2017) fabricated $LiClO_4$-PEO based ECD as an electrochromic layer, WO_3 film was coated by thermal evaporation, as ion storage layer TiO_2 film was coated by sol-gel dip coating method and the electrolyte layer $LiClO_4$/PEO/PC (1,3,3) were used. Optical modulation of 65% and 90k cycle stability were determined (Tang et al., 2017). The effects of SiO_2 and ITO nanoparticles on the electrochromic properties of polymer electrolytes were investigated (Pehlivan et al., 2014).

WO_3 is the most promising among electrochromic materials. Coloration occurs with the entry of ions into the WO_3 lattice, and bleaching occurs with the exit of the ions (Cremonesi et al., 2004). Adding metal nanoparticles such as Au, Ag and Pt enhances the coloration efficiency and durability of WO_3 nanoparticle films (Hoseinzadeh et al., 2017). hBN nanoplates improve mechanical properties, ionic conductivity and thermal stability in compassion bulk hBN microparticles (Hyun et al., 2019). Electrolytes consisting of PEO/LiTFSI/h-BN show high ionic conductivity. The PEO/LiTFSI/h-BN electrolyte has better cycling stability (140 cycles) than PEO/LiTFSI without h-BN electrolyte (39 cycles) (Li et al., 2020).

The preparation methods are very sensitive to nanostructures. Also, there is a fragility of nanostructures and the deterioration of their structures when used with ECD devices with gel electrolytes (Xie et al., 2019).

This study aims to fabricate of cost effective ECDs consisting of WO_3 nanoparticles, polymer electrolyte without plasticizer such as propylene carbonate thin films by sol gel process, determining hBN nanoparticles effects on response times of these fabricated ECDs.

To the best of our knowledge, WO_3/PEO-LiTFSI-hBN without propylene carbonate-based ECD has hitherto been unexplored for electrochromic applications.

2. EXPERIMENTAL SECTION

2.1. Preparation of WO_3 solutions with hBN and without hBN nanoparticles

WO_3 nanoparticles were dissolved with isopropanol (IPA) and deionized (DI) water (1:1:1 ratio) and the solution was mixed with a magnetic stirrer for 3 h at room temperature. For preparing the WO_3 solution with hBN, %2 hBN nanoparticles were added to the solution.

2.2. Preparation of PEO-based Polymer Electrolyte with and without hBN

LiTFSI was dissolved in acetonitrile (ACN) at room temperature for 1 h. After adding PEO to the solution, it is mixed for 5 hours. To prepare polymer electrolyte solution with hBN, 1% hBN nanoparticles were added.

2.3. Fabrication of Four Types of Electrochromic Devices

ITO/glasses were cleaned with acetone, ethanol, and IPA, respectively for 5 minutes in an ultrasonic cleaner. WO_3 solutions were spin-coated on conductive transparent ITO-glass at 2000 rpm for 20 seconds and annealed at 100 °C for 10 min. This process was adapted from Jeong (2021) to a thickness of 1 μ±0.1 (Jeong et al., 2021). Polymer electrolytes were dip coated at a speed of 1 mm/s on conductive transparent ITO-glass substrates and annealed at 100 °C for 10 min. These two processes are repeated three times. This process was adapted from Zhang et al. (2015) to a thickness of 30 μ±2. WO_3 and polymer electrolyte thin films were sandwiched. Edges of ECDs were sealed with silicon guns so humidity that disturbs devices was prevented. Four types of ECDs were fabricated. WO_3 thin films were fabricated with hBN and without hBN by sol-gel spin coating method and polymer electrolytes were fabricated with hBN and without hBN by sol-gel dip coating method. They were sandwiched in four configurations as given in Table 1.

Table 1: Four configurations of ECDs.

Device	Cathode	Electrolyte
ECD1	WO_3/hBN	PEO/LiTFSI/ hBN
ECD2	WO_3	PEO/LiTFSI/hBN
ECD3	WO_3/hBN	PEO/LiTFSI
ECD4	WO_3	PEO/LiTFSI

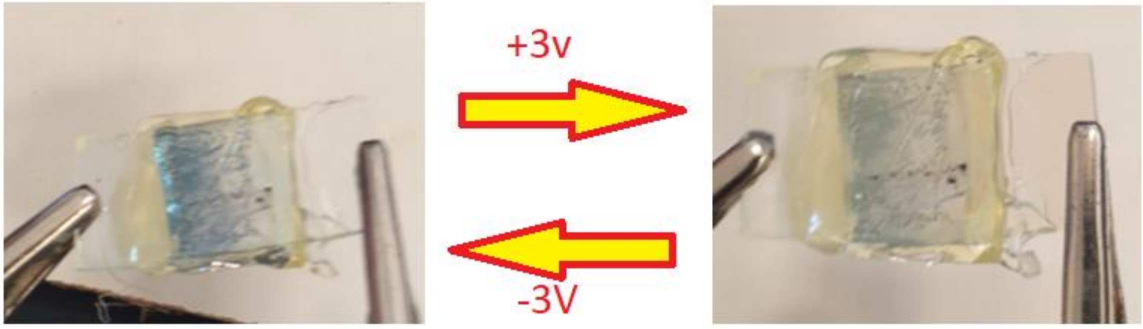

Figure 1: Fabricated ECD based on WO_3 with hBN, polymer electrolyte without hBN.

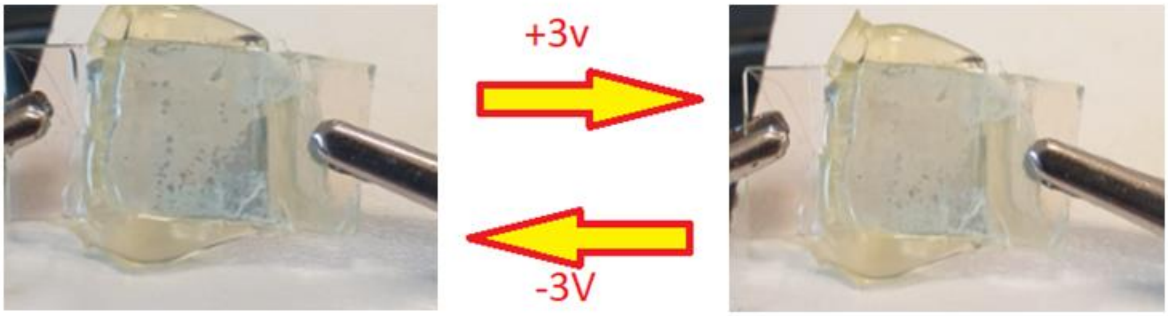

Figure 2: Fabricated ECD based on WO_3 without hBN, polymer electrolyte without hBN.

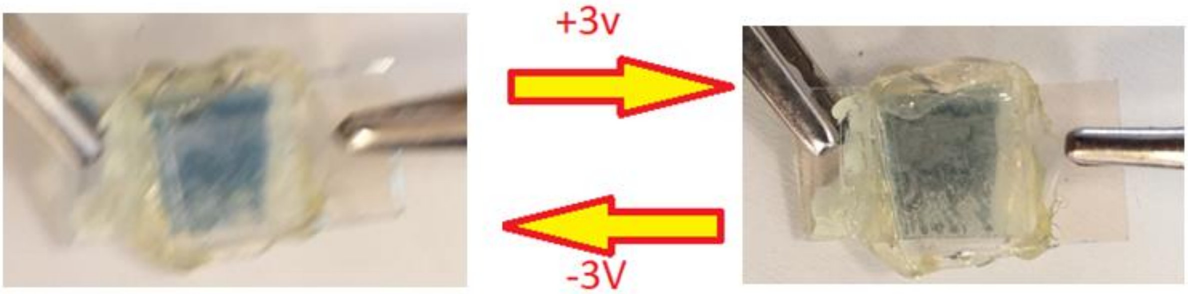

Figure 3: Fabricated Electrochromic Device based on WO_3 without hBN, polymer electrolyte with hBN.

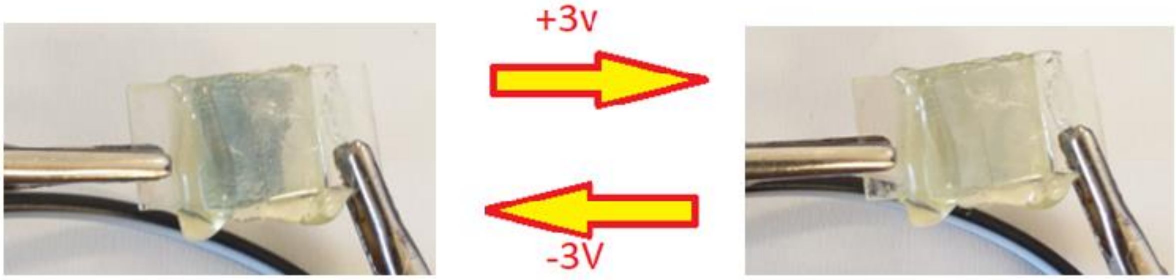

Figure 4: Fabricated Electrochromic Device based on WO_3 with hBN, polymer electrolyte with hBN.

3. RESULTS AND DISCUSSIONS

3.1. Scanning Electron Microscopy (SEM) Results of the WO_3 and Polymer Electrolyte Thin Films

Figure 5 shows SEM images of thin films. Figure 5a shows that the WO_3 thin film is highly porous with a large active surface area. Figure 5b shows a polymer electrolyte thin film that has a smooth surface and clumps of hBN embedded unsmooth.

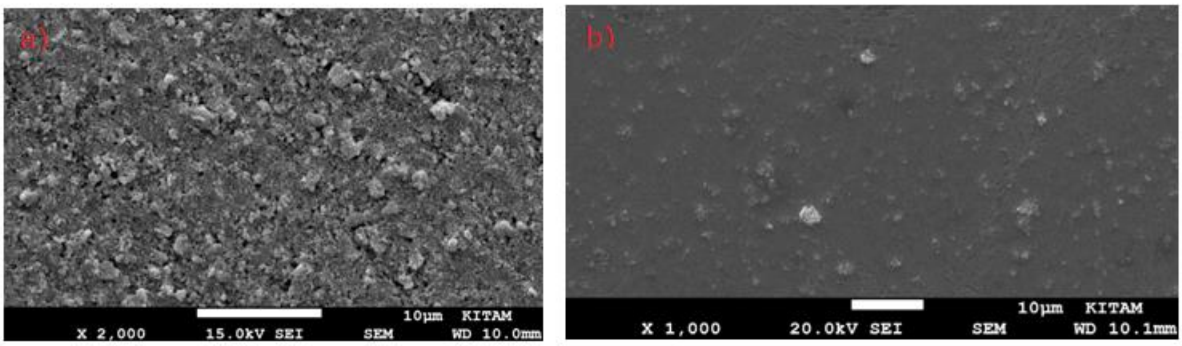

Figure 5: SEM Image of WO_3 at 2 kx and polymer electrolyte thin film at 1 kx.

Figure 6 shows the EDX (Energy Dispersive X-Ray) spectra of thin films. Figure 6 a provides evidence for the chemical quality of WO_3 thin film. The EDX spectrum exhibits the characteristic peaks of Oxygen, Tungsten, Indium and Tin in the film. Tungsten and Oxygen peak from the Tungsten oxide phase and Indium and Tin peak from the ITO phase. However, the absence of any other peaks except these elements is evidence of the chemical quality of grown films without any elemental impurities. Figure 6b displays the EDX elemental analysis of polymer electrolyte. Au peaks are observed In EDX spectra. Au coating of samples was required in the SEM to enable the imaging of samples. Carbon and Oxygen are obtained from the PEO phase; Fluorine and sulfur elements are obtained for the formation of LiTFSI. At the same time, relatively smaller amounts of Pd and Cu are observed.

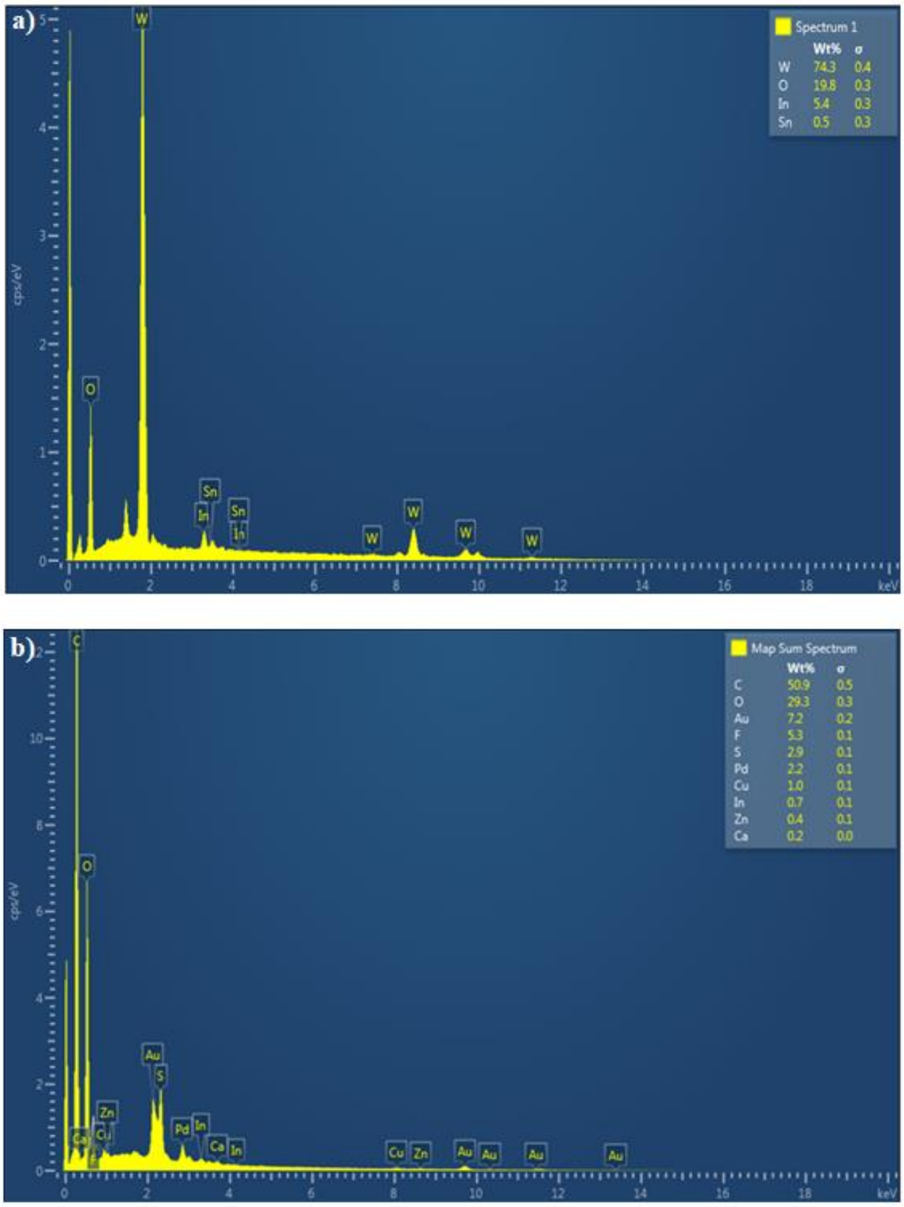

Figure 6: EDX spectrum of a) WO_3, b) polymer electrolyte thin film.

3.2. Fourier Transform Infrared Spectroscopy (FTIR) Results of Polymer Electrolyte Thin Films

FTIR spectrum of polymer electrolyte thin film is displayed in Figure 7. FTIR results show the bands appeared around 3500-3600 cm^{-1} were assigned for O-H group and intermolecular bonding. The vibrational frequency corresponding to CH_2 rocking mode appears at 700-800 cm^{-1}. For asymmetric SO_2 stretching mode and S-CF_3 bonding mode, wavenumbers are spotted at 1447 and 2250 cm^{-1}. For the C-SO_2-N bonding mode of LiTFSI wavenumber is at 1377 cm^{-1}. N-S bonding mode is obtained at 3170 cm^{-1} wavenumber. C-H bonding mode exists between 2900-3000 cm^{-1} wavenumbers.

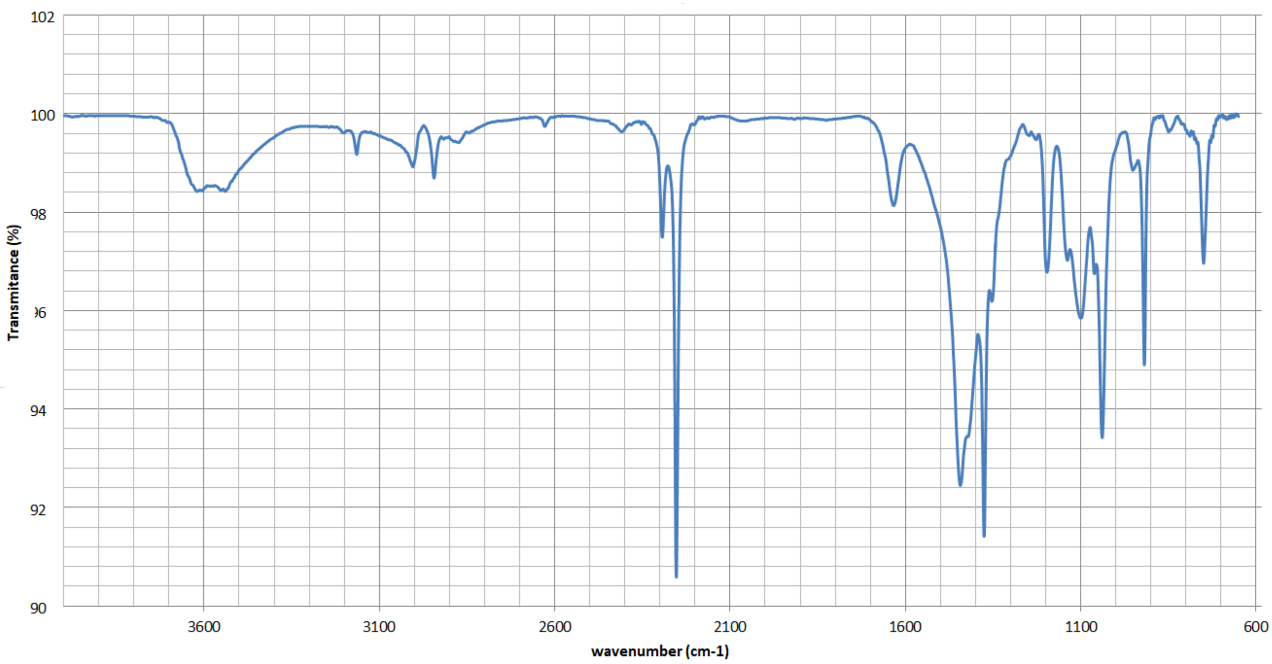

Figure 7: FTIR spectrum of polymer electrolyte with LiTFSI.

3.2. UV-Visible (UV-Vis) Spectroscopy Results of Polymer Electrolyte and WO_3 Layer

UV-Vis spectra of polymer electrolyte layer and WO_3 cathode layer are shown in Figure 8. The UV-Vis spectrum of polymer electrolyte thin film for the wavelength range of 300 and 800 nm is displayed in Figure 8a. It is clear that the transparency of the film increases with increasing wavelength. Transparency ranges between 80-90% which is ideal for ECDs. In Figure 8b, The UV-Vis image of a WO_3 thin film for wavelength range of 300 and 800 nm is displayed. Transmittance of WO_3 coated on PET-ITO increases with increasing wavelength. From the transmission spectrum, it is clear that the transparency of the film increases with increasing wavelength. Transparency of the film is suitable for electrochromic devices and similar to Zhang et al. (2022).

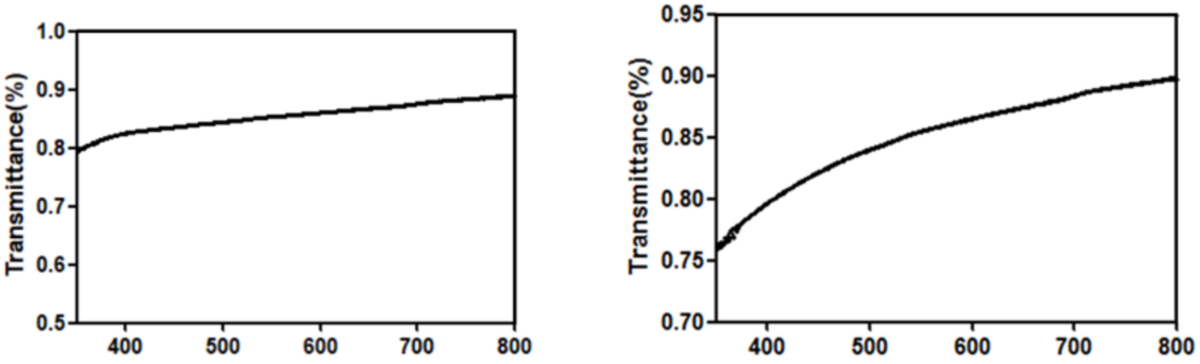

Figure 8: UV-Vis spectra of polymer electrolyte and WO_3 layer. The X axes are wavelength.

3.2. X-ray Diffraction (XRD)

XRD technique was used to obtain the crystallographic structure of WO_3-coated on PET-ITO. WO_3 nanoparticles that were purchased from Nanografi company have a high purity of 99.99% in the orthorhombic phase and a size between 20-60 nm. In Figure 9, XRD spectrum of WO_3 thin film is displayed. Strong and sharp diffraction peaks are observed at 2θ = 23.1°,23.6°, 24.4°, 26.5°, 28.8°, 33.3°,34.2°, 41.7°, 53.5°, 55.9°, all of which are associated to the (002), (020), (200), (120), (112), (022), (202), (222), (400) and (420) crystalline planes of the orthorhombic phase of WO_3 with a good crystallization which is important for stability.

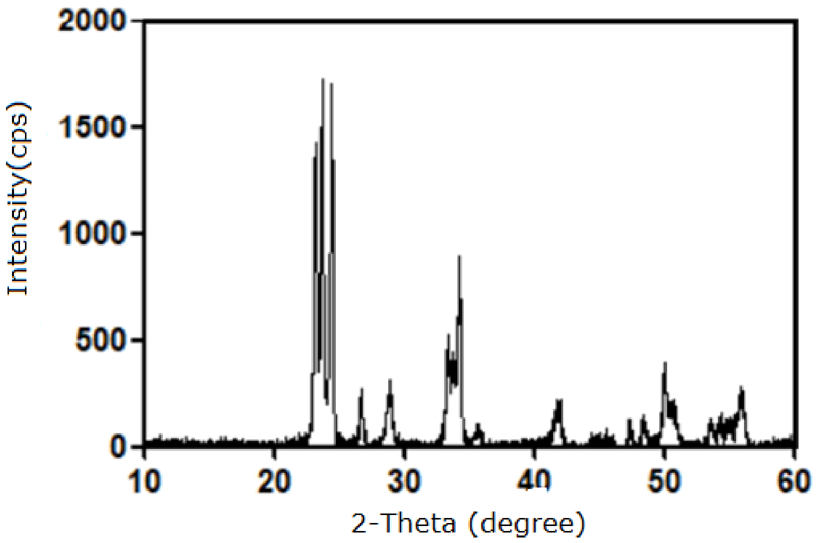

Figure 9: XRD spectrum of WO3 thin film.

3.3. Performance of ECDs

The bleaching and coloring time of fabricated ECDs in this study was obtained in nearly 1-2 seconds. Reasonably good response times are obtained compared to the coloration and bleaching times in the literature. Glass/ITO/hBN-WO_3/hBN-PEO Electrolyte/ITO/Glass configuration of ECD cycled 60 times. After 60 cycles, the device coloring time changed to 2-3 seconds and bleached times changed to 30 seconds.

In Table 2, measured with standard deviation of these values, coloring (t_c) and bleaching (t_b) times of fabricated ECDs with hBN and without hBN are displayed. Results were determined by taking the average of 10 cycles of ECDs. Figure 9 shows adding hBN for both electrolyte and electrochromic layer decreases coloring (t_c) and bleaching (t_b) times of ECDs

Table 2: Coloring and bleaching times of four configurations of ECDs.

Sample	Cathode	Electrolyte	t_c (s)	t_b (s)	STD (t_c (s))	STD (t_c (s))
ECD1	WO_3 with hBN	PEO/LiTFSI/ hBN	1.15	1.15	0.24	0.24
ECD2	WO_3	PEO/LiTFSI/hBN	1.65	1.51	0.21	0.44
ECD3	WO_3 with hBN	PEO/LiTFSI	2.27	1.97	1.43	1.17
ECD4	WO_3	PEO/LiTFSI	1.50	2.14	1.28	1.49

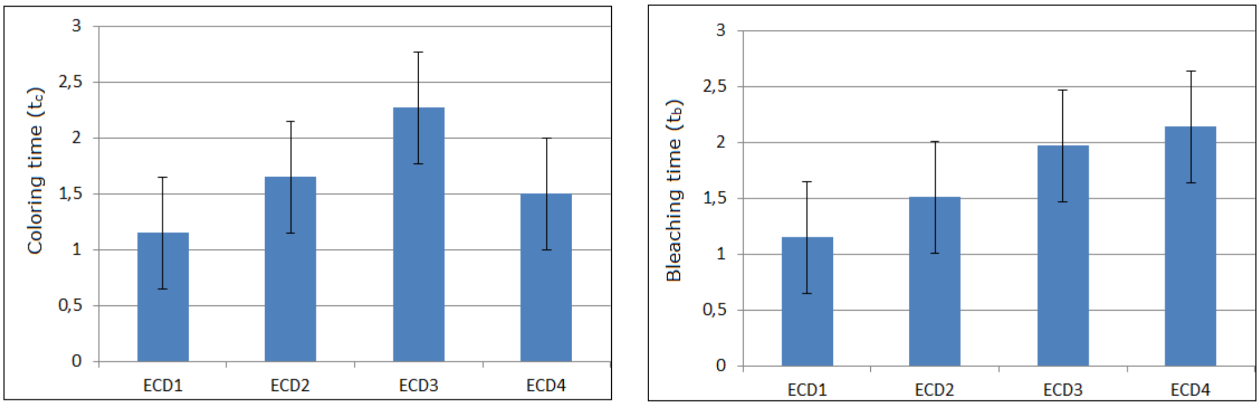

Figure 10: Graphics of coloring and bleaching times of four configuration of ECDs.

The transmittance of ECD1 was measured by a fabricated Arduino-based electronic device in our thin film laboratory. In Figure 10, the transmittance of ECD1 is displayed for 10 s switching time. Coloring (t_c) and bleaching (t_b) times were obtained as a few seconds. Transmittance changes from 64 to 59% or vice versa. The results of transmittance in Figure 10 are consistent with the results of Xie (2019).

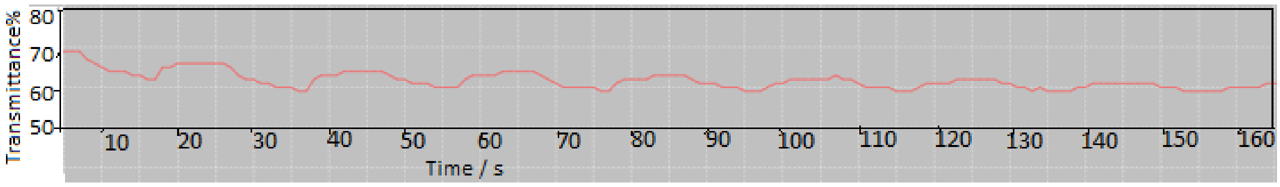

Figure 11: Transmittance over time of fabricated ECD1 for 10 seconds interval switching.

4. CONCLUSION

All solid-state electrochromic devices (ECDs) without plasticizers, such as propylene carbonate, were fabricated by the sol-gel spin coating method. PEO-based polymer electrolytes and WO_3 solutions with and without hBN were prepared successfully. WO_3 solution and polymer electrolyte were spin and dip coated respectively on ITO-glass substrate. After annealing, thin films were sandwiched and four types of ECDs were fabricated. Colored and bleached states were obtained by giving -3 V and +3 V voltage from the edges. The bleaching and coloring time of ECD1, ECD2, ECD3 and ECD4 are 2.14-1.5, 1.97-2.27, 1.51-1.65, and 1.15-1.15 seconds, respectively. These results show that hBN nanoparticles for both electrochromic and electrolyte layers decrease the switching times. The fast bleaching and coloring times are obtained from ECD1. ECD1 was cycled 60 times. After 60 cycles, the device coloring time changed to 2-3 seconds and bleached times changed to 30 seconds.

For the characterization of WO_3 cathode and polymer electrolyte layers, SEM, EDX, UV-Vis and FTIR characterization techniques were used. SEM results show that smooth and homogenous thin films are obtained. EDX spectrum shows chemical composition. EDX results prove the chemical quality of grown layers without any elemental impurities. UV-Vis results show that between 300-800 nm range polymer electrolyte and WO_3 cathode layers have enough transmittance for ECDs. The WO_3 film coated on ITO/Glass substrate exhibits %85 transmission at 550 nm. Chemical bonds of the polymer electrolyte layer are determined with FTIR.

5. REFERENCES

Cremonesi, A., Bersani, D., Lottici, P. P., Djaoued, Y., Ashrit, P. V. (2004). WO3 thin films by sol–gel for electrochromic applications. *Journal of Non-Crystalline Solids 345&346*, 500-504.

Eren, E. (2018). Li+ doped chitosan-based solid polymer electrolyte incorporated with PEDOT:PSS for electrochromic device. *Journal of the Turkish Chemical Society*. *5*(3), 1413-1422.

Fu, X. (2010). Polymer electrolytes for electrochromic devices. *Electronic and Optical Materials*, 471-523.

Fullerton-Shirey, S. K., Maranas J. (2010). Structure and Mobility of PEO/LiClO4 Solid Polymer Electrolytes Filled with Al2O3 Nanoparticles. *J. Phys. Chem. C, 114*, 9196–9206.

Hoseinzadeh, S., Ghasemiasl, R., Bahari, A., Ramezani, A. H. (2017). The injection of Ag nanoparticles on surface of WO3 thin film: enhanced electrochromic coloration efficiency and switching response. *J Mater Sci: Mater Electron*, *28*, 14855–14863.

Hyun, W. J., Moraes, A. C. M., Lim, J. M., Downing, J. R., Park, K. Y, Tan, M. T. Z., Hersam, M. C. (2019). High-Modulus Hexagonal Boron Nitride Nanoplatelet Gel Electrolytes for Solid-State Rechargeable Lithium-Ion Batteries. *ACS Nano*, *13*, 9664-9672.

Jeong, C.Y., Kubota, T., Chotsuwan, C., Wungpornpaiboon, V., Tajima, K. (2021) . All-solid-state electrochromic device using polymer electrolytes with a wet-coated electrochromic layer. *Journal of Electroanalytical Chemistry*, *897*, 115614.

Li, Y., Zhang L., Sun Z., Gao G., Lu S., Zhu M., Zhang Y., Jia Z., Xiao C., Bu H., Xi K., and Ding S. (2020) . Hexagonal boron nitride induces anion trapping in a polyethylene oxide based solid polymer electrolyte for lithium dendrite inhibition. *J. Mater. Chem. A*, *8*(19), 9579–9589.

Pehlivan, İ. B., Marsal, R., Pehlivan, E., Runnerstrom, E. L., Milliron, D. J., Granqvist, C. G., Niklasso, G. A. (2014). Electrochromic devices with polymer electrolytes functionalized by SiO2 and In2O3:Sn nanoparticles: Rapid coloring/bleaching dynamics and strong near-infrared absorption. *Solar Energy Materials & Solar Cells, 126*, 241-247.

Solovyev, A. A, Zakharov, A. N., Rabotkin, S. V. Kovsharov, N. F. (2016). Electrochromic Device with Polymer Electrolyte. *Journal of Electronic Materials*, *45*(8), 3866-3871.

Tang, X., Chen, G., Liao, H., Li, Z., Zhang, J., Luo, J. (2020). Unveiling mechanical degradation for a monolithic electrochromic device: Glass/ITO/WO_3/$LiClO_4$ (PEO)/TiO_2/ITO/glass. *Electrochimica Acta*, *329*, 135182.

Xie, Z., Liu, Q., Zhang, Q., Lu, B., Zhai, J., Diao, X. (2019) . Fast-switching quasi-solid state electrochromic full device based on mesoporous WO3 and NiO thin films. *Solar Energy Materials and Solar Cells*, *200*, 110017.

Zhang, B., Luo, J., Chen, Z., Wu, L., Li, J., Tian, Y., Liu, S. (2022). Synthesis, characterization and dual-band electrochromic properties of Nb-doped WO3 films. *Journal of Electroanalytical Chemistry*, 918.

Zhang, Y., Zhao, Y., Gosselink, D., Chen, P., (2015). Synthesis of poly(ethylene-oxide)/nanoclay solid polymer electrolyte for all solid-state lithium/sulfur battery. *Ionics*, *21*, 381-385.