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# **Textile Based Three-Layer Robust Flexible and Stable Electrochromic Display**

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**ABSTRACT** The textile-based electrochromic (EC) display which has been developed and presented in this article, is very compact, robust, flexible, stable, efficient, economical, and inclined to biocompatibility. The developed textile display is having only three-layer over conventional seven layers patented electrochromic structures. It is also very efficient, as it can perform its functionality even after 2500 cycles of a run and 1500 times of bending. The innovative and simplified structure of the EC device has been developed with only 3 layers, including the displaying electrode, the electrolyte container, and the counter electrode. The conductive polymer PEDOT:PSS used here as a conductive and electrochromic material, is coated on the textile substrate to perform as one side of the electrode for the asymmetric arrangement of the electrochromic device. The experiment has also been done to find out the best possible textile fabric to serve as the optimal electrochromic container. The biocompatible H<sub>3</sub>PO<sub>4</sub> gel drenched in the semi-permeable membrane has been used as an ion transfer medium for the electrochromic display. This biocompatible ion transfer medium is sandwiched in between the electrochromic displaying electrode (PEDOT:PSS coated on fabric) and aluminum sheet (counter electrode) for making this handmade crude electrochromic display. The investigation of the EC display functioning has been observed through cyclic voltammetry within the life cycle run. The performance of the device has also been investigated in real-life conditions, by providing just  $\pm 2.0 \text{ V}$  DC power. The other possibility is shown in our article to deposit the PEDOT:PSS compound on the textile substrate was to coat directly the yarns and then to use them into the weaving process to produce the displaying electrode. By this technique, it would also be possible to develop hybrid displays made of structures containing knitted or woven side-emitting optical fibers and our electrochromic display structure, locally.

**INDEX TERMS** Electrochromism, PEDOT:PSS, simplified 3-layer structure, textile display, electrochromic display, sustainable design, flexible display, smart textile.

#### I. INTRODUCTION

The coming era promises everything would be fully automatic whether it belongs to the defense sector, industry, or normal household equipment. If the focus is only on automatization in colorization and appearance, then the defense personal will wear a uniform that could produce full camouflage from the enemy during the war. The car industry is going to produce cars that will be driverless and full of the automated comfortable soft-touch electrochromic display. The home decor wall will change the color as per the owner's desire, similarly, the change in color of wearing clothes and many more. The chromism is a very fundamental

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phenomenon where reversible color changes occur in the response to external stimuli on chromic materials and depend on the external stimuli the chromism name apportioned [1]. The chromism, where the change, evocation, or bleaching of color occurs because of the electron-transfer (redox) process or by providing sufficient electrochemical potential is called Electrochromism and this transition happens in Electrochromic materials (viologens, transition metal oxides (WO<sub>3</sub>, MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>), metal hexacyanometallates, conducting polymers, etc.) [2]–[6].

In electrochromic research, the conductive polymers are an eye-catching candidate due to its higher conductivity and redox abilities, and especially PEDOT:PSS (poly(3, 4ethylenedioxythiophene) polystyrene sulfonate) influenced a lot because of its stable reversible electrochemical behavior



with very high conductivity (up to 1000 S/cm) and stable redox window [7], [8]. Due to a lot of favorable properties of PEDOT:PSS as an electrochromic material, it is suitable for the incorporation as an electrochromic material [9]. As shown in Figure 1, the PEDOT:PSS is a mixture of two ionomers viz. sodium polystyrene sulfonate (carries negative charges and part of sulfonyl group) and poly (3,4ethylenedioxythiophene) (carries positive charges and part of polythiophene) [10], [11]. With accountancy of PEDOT:PSS, a lot of research work is going on in chromism and especially on electrochromism for supporting the next generation of displays [12], [13]. In the quest for the best electrochromic display device (flexible, robust, lower switching time, sharp color change, stable, longer lifetime, biocompatible, and economically viable), the researchers are trying to achieve an optimized minimum layer structure in a single electrochromic cell. A flexible fabric substrate is also required as the best electrochromic material for (low redox potential and switching time), instant and sharp color change, and low power and biocompatible electrolyte.

The switching time is one of the prominent issues with electrochromic devices. The researchers have done a lot of work on the electrochromic layer and electrolytes for improving the switching time. The lithium-based electrolyte could be a better option (because of lower size and higher mobility of Li<sup>+</sup> ions) such as Lithium-based sol-gel, but at the same time, it provokes toxicity. The H<sub>3</sub>PO<sub>4</sub> gel electrolyte has inorganic H<sup>+</sup> ions, which is also having higher mobility with maintaining its biocompatibility. One the other side, the PEDOT:PSS is one of the best candidates for faster switching time. Generally, the electrochromic device contains seven layers in a sandwich structure with dedicated functionality for each layer [14]. The researchers are trying to reduce the number of layers for minimizing the effort and cost. Mecerreyes D. et al. 2004 worked with conductive polymer and reduced the number of layers of the electrochromic device from seven to five [15]. F. M. Kelly et al. 2013 proposed a four-layer sandwich structure by reframing the entire electrochromic device module [16].

In this article, just a three-layer structure with a very simple arrangement of the displaying electrochromic electrode, the electrolyte container layer, and the counter electrode is proposed. The device is very much flexible and robust as it has a textile substrate (polyester 140 dtex fabric), that is biocompatible due to 1 M phosphoric acid gel electrolyte and PEDOT:PSS conducting polymer as electrochromic material. The device stability is so high that even after 2500 cycles run, it can perform customarily. In the subsequent unit of this paper, we briefly discussed the device assembling process, electrochemical testing (Cycle Voltammetry), and life cycle estimation.

#### **II. MATERIALS, METHOD AND DEVICE STRUCTURE**

Generally, the electrochromic device contains four basic ingredients as an electrochromic material, an electrolyte, conducting electrodes, and a substrate. Here, PEDOT:PSS has been used as an electrochromic material, H<sub>3</sub>PO<sub>4</sub> gel as an electrolyte, an aluminum sheet as a counter electrode, and a textile fabric as a substrate for an asymmetric arrangement of the electrochromic device (Figure 1a). For the preparation of the electrochromic solution, the PEDOT:PSS (structure shown in Figure 1b) was mixed with demineralized water (two times in volume ratio) (which is optimized through several iterations) and stirred this mixture for approximately 10 minutes. In this mixture, 5% Dimethyl sulfoxide was dropwise added (in volume percentage) and continuously stirred the mixture for 10 minutes more. A beneficial part of this solution is that it can perform a dual operation, first as an electrochromic layer, and second as the conductive layer (because of very high electrical conductivity). Therefore, the ability of this solution to minimize the layers in a crude handmade electrochromic device has been accomplished. The typical transparent conductive layer which is an essential part of the conventional electrochromic device is removed in this arrangement.

The first step of the display production was to perform the coating of this solution onto the substrate. Two different kinds of procedures to implement and investigate this coating were performed. The first procedure was to directly coat on the readymade fabric and to perform electrochromic device manufacturing and testing. The second procedure consists in the direct coating on the yarn. Then, the weaving was performed to produce a fabric from a coated yarn and further to manufacture the electrochromic device and to test it. Here, both processes are described in a brief one by one. In the first process, several readymade fabrics have been chosen made of different materials (synthetic, natural fiber-based and composites) with a thickness suitable for coating by the EC compound. The different fabrics behave differently for making efficient electrochromic electrode as per their inbuilt nature such as hydrophobicity, hydrophilicity, inbuilt fabric capillaries (pore size), the thickness of the fabric, etc. It was observed that a semi hydrophobic fabric with the highest possibilities of inbuilt fabric capillaries (for the higher surface area) and moderated thick (140-200 dtex) perform better. After a lot of iterations and comparison of different fabrics, the polyester-based flex printing fabric of 140 dtex has been selected for working as a substrate for our electrochromic displaying electrode. The synthesized electrochromic solution was coated on this 140 dtex polyester-based flex printing fabric. The coating has been done by manual dipping of a 2 cm x 2 cm polyester fabric, several times (3 to 4). For proper drying, this coated fabric was placed in an oven at 100 °C for 20 minutes. The dried PEDOT:PSS coated fabric appearance was light grey (Figure 1c). It was supposed to work as an electrochromic material coated displaying electrode (one side) for the asymmetric arrangement of the electrochromic device. Concerning the electrolyte container layer, the gel electrolyte has been prepared by mixing 2 g of Poly (vinyl alcohol) in 1 M H<sub>3</sub>PO<sub>4</sub> in 40 ml of DI water, and this mixture was continuously stirred for 2 hours at 85 °C temperature. After 2 hours, the mixture became completely transparent



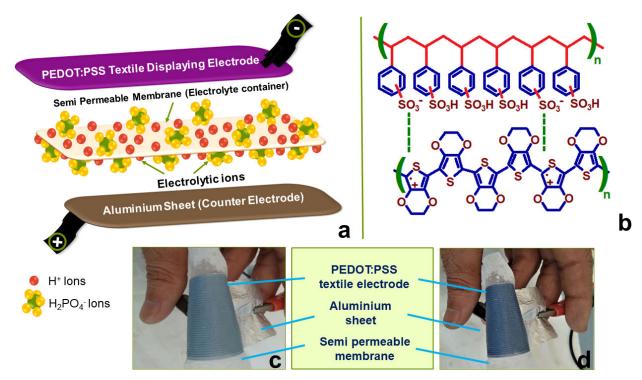


FIGURE 1. Electrochromic Device Structure and its flexibility. (a) Structure of the simplest electrochromic device developed in the lab. (b) Chemical Structure of PEDOT:PSS. (c) The reduction stage of the lab-made electrochromic device (in folded structure for showing its flexibility) by applying +2.0V DC supply. (d) The oxidation stage of the same folded lab-made electrochromic device by applying -2.0 V DC power supply.

and viscous. This signified that the transparent electrolyte gel was formed [17], [18], and ready to be poured to the semipermeable membrane container layer.

This new generation of three-layer electrochromic devices contains an electrochromic displaying electrode (PEDOT:PSS coated polyester fabric), a semipermeable membrane (Tissue paper) representing the electrolyte container and a counter electrode (Aluminum sheet). The semipermeable membrane used for the restriction of electrons movements inside the device and bound the electrons to move outside the circuit from this electrochromic device. The semipermeable membrane (tissue paper) was drenched in H<sub>3</sub>PO<sub>4</sub> gel, for working as an ion transfer medium for the electrochromic device. The electrolyte dunked semipermeable membrane sandwiched in between the two electrodes PEDOT:PSS coated polyester fabric and aluminum sheet. This simple structure forms a crude level of the handmade device, which can actively perform an electrochromic operation with minimum resources. The silver paste was deposited at the one end of PEDOT:PSS electrode for proper connection to the outside power supply. For an investigation of its functionality, the  $\pm 2.0$  V DC power supply has been applied to this handmade crude device. The positive terminal of the supply has been connected to the aluminum electrode and the negative terminal to its counterpart electrochromic displaying electrode. After switching on the power supply, the electrochromic electrode color changed to become dark blue over light grey (Figure 1d), this is called the oxidation stage. When the connection is reversed with the same voltage, the color is also reversed by becoming light grey over dark blue of the electrochromic displaying electrode; this stage is called the reduction stage. It can be observed in Figure 1c and d that the device is highly flexible as the device is completely folded even though it performs as usual.

The device functioning can be observed in the video supplementary 1 in detail. Figure 1a shows the schematic arrangement of the designed electrochromic device, whereas Figures 1c & d show the folded handmade physical electrochromic device with reduction and oxidation stages. Further, observation has been performed by electrochemical testing such as the Cyclic Voltammetry analysis (CV) and a life cycle analysis. The cyclic voltammetry analysis executed from -2.0 V to 2.0 V voltage range at different scan rates, ranging from 5 mV/sec to 500 mV/sec and life cycle analysis has been done on the same voltage range with 50 mV/sec scan rate within 2500 run of the cycles on Zive SP1 Electrochemical workstation instrument.

On the same note for the second process of the electrochromic displaying electrode making by yarn coating and weaving, different yarns have been collected and the direct PEDOT:PSS coating has been performed on them. Finally, the fabric has been made through the weaving process. The remaining process of electrochromic device making and testing is similar to the prior elaborated process. The yarn direct coating process has been carried out on the continuous roll to roll process shown in Figure 2. Figure 2a shows the block



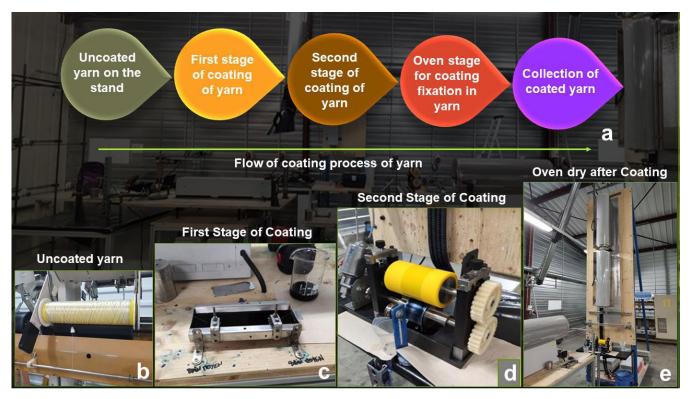


FIGURE 2. Complete setup of electrochromic PEDOT:PSS solution coating on yarn. (a) Block diagram flow of PEDOT:PSS coating process on yarn. (b) Uncoated yarn bobbin. (c) The first stage of PEDOT:PSS coating by filled tray-based dip coating. (d) The second stage of the coating by roller based system. (e) 180 circ C constant temperature oven for drying and fixing of coating and the coated yarn bobbin on the right backside of the oven.

diagram of the yarn coating process flow from uncoated yarn to dried coated yarn. Figures 2b to 2e show the images of each stage, defined in the block diagram of Figure 2a. From left to right, there is a yarn stand containing the uncoated yarn bobbin (Figure 2b), then there are two stages of PEDOT:PSS coating, first filled tray-based, and second roller based coating shown in Figure 2c and 2d respectively. Further, the vertical oven for drying the coated yarn is on the rightmost side (figure 2e), and finally, the collection of coated yarn on the right backside of the setup and oven. In this setup, a yarn coating has been performed with a coating speed of 10 m/min. The first stage of dip coating was performed in an electrochromic PEDOT:PSS based solution which was filled in a tray (shown in Figure 2c), and the second stage in a roller based coating (shown in Figure 2d) which is also filled with PEDOT:PSS based solution. The yarn passes 5 times through the vertical oven at 180 °C atmosphere for drying and fixing of the coating.

The yarns which have been selected for the coating were: 140 dtex polyester unwashed yarn, 140 dtex polyester washed yarn, 167 dtex polyester textured yarn, and 235 dtex polyamide yarn based on the previous experiment of textile fabric coating and testing. For the optimization of the best-suited concentration of PEDOT:PSS solution coating, the different PEDOT:PSS concentration solutions (1.5 times, 2.0 times, and 2.5 times diluted) have been selected. The electrochromic solution synthesis process was similar to the

**TABLE 1.** Experiment combinations (E1-E12) of yarns and PEDOT:PSS solutions for yarn coating process.

	Yarn				
Parameters		140 dtex Polyester Washed	140 dtex Polyester Unwashed	167 dtex Polyester Textured	235 dtex Polyamide
PEDOT:PSS Dilution Ratio	1.5 times	E1	E2	E3	E4
	2.0 times	E5	E6	E7	E8
	2.5 times	E9	E10	E11	E12

prepared one during the fabric coating process. The coating was performed on each yarn by all these different concentrated PEDOT:PSS solutions. Overall, 12 combinations (named E1–E12) of different electrochromic coated yarns came into existence (summarized in Table 1).

The simple weaving (plain pattern) was done by ARM Handloom Weaving Machine for all twelve possible combinations of coated yarns (Figure 3a). These coated yarn woven fabrics would act directly as an electrochromic displaying electrode for our lab made EC display devices. Figure 3b is the image of 235 dtex polyamide yarn with a coating of 1.5 times diluted PEDOT:PSS solution (E4) and for the control and comparison, the similar yarn fabric without any coating is also woven which is shown in figure 3c. All twelve



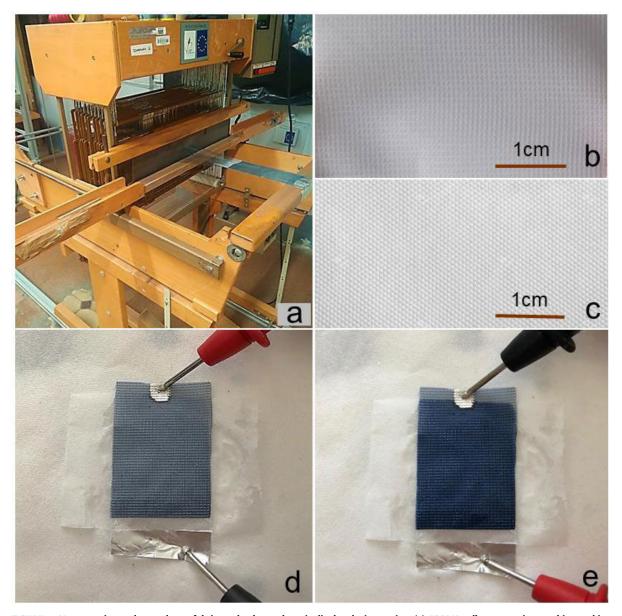


FIGURE 3. Yarn weaving and coated yarn fabric made electrochromic display device testing. (a) ARM Handloom weaving machine and its working. (b) PEDOT:PSS coated yarn fabric after weaving. (c) Non coated yarn fabric after weaving. (d) Reduction (color change) in PEDOT:PSS coated yarn fabric made an electrochromic device. (e) Oxidation (or reverse the color change) in PEDOT:PSS coated yarn fabric made electrochromic device.

electrochromic devices have been fabricated, similar to the previously explained electrochromic device fabrication process. The size of the devices was also the same (2 cm x 2 cm) for all woven fabrics dedicated to serving as electrochromic displaying electrodes, and a similar process of device testing was accomplished (by giving  $\pm 2.0$  V supply and observing the color change).

The aforesaid materials are purchased from different companies and brands such as PEDOT:PSS (Clevios PH 1000) from Heraeus Deutschland Germany, Phosphoric acid, aluminum sheet (0.001in), Dimethyl sulfoxide, Poly (vinyl alcohol) from Sigma Aldrich, and Silver paint (RS 186-3593) from RS components.

## **III. RESULTS AND FUTURE SCOPE**

It has been observed that out of twelve combinations of devices, two of them having 1.5 times ratio diluted PEDOT:PSS solution coated on 167 dtex polyester textured yarn (E3) and 235 dtex polyamide yarn (E4) were showing the effect of electrochromism. The more prominent observable effect could be seen only in an E4-based coated device. Probably, the fabrics which were having the yarn coating at 2 and 2.5 times ratio diluted PEDOT:PSS solution (E5 - 12) were not able to show the electrochromic effect, because of the very low amount of PEDOT:PSS on the surface of the yarn. Perhaps, E1 & E2 (140 dtex washed and unwashed polyester yarns) combinations out of four combinations which were



having the 1.5 times ratio diluted PEDOT:PSS solution coating was not able to show the effect of electrochromic nature, because of higher hydrophobicity nature and low capillary action of 140 dtex polyester yarn, as compared to 167 dtex textured yarn and 235 dtex polyamide yarn. The 235 dtex polyamide yarn is thicker, so it has a higher surface area to absorb a higher amount of electrochromic solution. A similar prospect has also been observed in coating color appearance as the 235 dtex yarn coated fabric was having darker grey color (due to the higher amount of PEDOT:PSS absorbance) as compared to other yarns. This higher amount of coating gives a chance to perform better electrochromic operations over others. Figures 3d and 3e show the electrochromic testing at ±2.0 V with a reversible color change (light grey to dark blue when +2.0 V and reversible when -2.0 V is applied). The complete electrochromic process of 235 dtex coated yarn device is shown in supplementary video 2. For comparison, the uncoated 235 dtex polyamide yarn fabric is also woven (Figure 3c) and a dip coating in PEDOT:PSS solution was performed (1.5 times ratio, 2.0, and 2.5 times ratio diluted), and further it has been dried in an oven (as performed in the first process). The three similar electrochromic devices (depend on concentration) have been fabricated and tested by providing a DC power supply. It has been observed that out of three, the two devices of 1.5 times and 2.0 times ratios diluted PEDOT:PSS coated electrodes were showing the effect of electrochromism. While comparing from the coated yarn fabric electrochromic device to a fabric coated electrochromic device, the fabric coated device was having much better performance (implying darker color change appearance during the reduction process). This is possibly happening, because the absorption of PEDOT:PSS in the fabric is higher due to capillary action. As a result, the yarn coating process is not impactful for further experiment process of making an electrochromic display device.

While performing the comparison between the 235 dtex yarn made fabric electrochromic device and 140 dtex readymade polyester-based flex printing fabric electrochromic device, the 140 dtex polyester-based flex printing fabric electrochromic device was much better in terms of reversible color change and switching timing. Therefore, in all further experiments and investigations, the 140 dtex polyester-based flex printing fabric electrochromic device has been used. The added advantage with the polyester-based flex printing fabric as it is economical, highly flexible, durable, thin, and biocompatible.

The CV analysis was carried out using the Zive SP1 Electrochemical workstation instrument with two-electrode systems. Figure 4a shows the CV performance on a voltage range of -2.0~V to +2.0~V at various scan rates ranging from 10 mV/sec to 500 mV/sec. Figure 4b is representing the CV analysis of the electrochromic device at the scan rate of 50 mV/sec, it can be observed that the two oxidation peaks at -0.3~V and 1.2~V and the corresponding two reduction peaks at 0.1~V and 1.5~V are visible. It shows the proper redox reaction happening in the electrochromic device, which

signifies higher stability. The peak currents of these four peaks increase with the increase of the scan rate (except at higher scan rates such as 300 and 500 mV/sec scan). It indicates that an electroactive polymer layer PEDOT:PSS is present on the electrode surface. The first oxidation peak (-0.3 V) is not so clear, especially for higher scan rates, but the 1.2 V peak and the corresponding reduction peaks at 0.1 V and 1.5 V (except 500mV/sec) are properly visible, even at high scan rates. The anodic and the cathodic peak currents depend linearly on the scan rate. It signifies that the electrochemical process is reversible. It may be observed that the current density and the coverage area are increasing as a scan rate is increasing. Yet, when the specific capacitance calculation is done, the specific capacitance decreases as the scan rate increases. This is possibly happening because of insufficient time available for ion diffusion at a faster scan rate. The specific capacitance (Cs) calculation is done from CV curve by using the given equation [17]–[19].

$$Cs = \int \frac{I(u) dt}{m} \times v \times \Delta V$$

where I is the oxidation or reduction current, m indicates the mass of the active electrode material, v is the scan rate, dt is time differential, and  $\Delta V$  indicates the voltage range of one sweep.

For the investigation of the stability of the electrochromic device, the run of 2500 cycles of CV analysis has been performed at a scan rate of 50 mV/sec. It can be observed in Figure 4c that the CV runs are not having many deviations in all cycles excepting for few outliers (probably due to connection noises). The CV cycles are retaining the initial cycle shape. It shows that the device is highly stable even at very long cycles of the run (2500). The specific capacitance is calculated for all the 2500 cycles and observed the retention property of the specific capacitance over the cycles. In Figure 4d, it can be observed that the electrochromic device can retain more than 75 % of the specific capacitance value even at 2500 cycles of the run. It is supporting the statement that the device is very stable even for the larger run-up to 2500 cycles. While performing the CV run up to 2500 cycles, the electrochromic device function of reversible color change was prominent visible and synchronized with CV during all the cycles.

The functioning of the display device synchronized with CV analysis has been shown in supplementary video 3. This analysis has been performed on a similar 2 cm x 2 cm laboratory-made crude electrochromic device by the cyclic run of CV at 100 mV/sec scan rate in the voltage range of -2.0 V to 2.0 V. It is suggestible that the proper observation of electrochromism of the device can be observed at lower scan rate, but at the same time switching time parameter should also be taken into consideration. That is why a 100 mV/sec scan rate has been considered (300 mV/sec also done and shown in supplementary video 4). During this investigation, the device was properly able to maintain its reversible color change property, even at the 2500<sup>th</sup> cycle of the run. It has

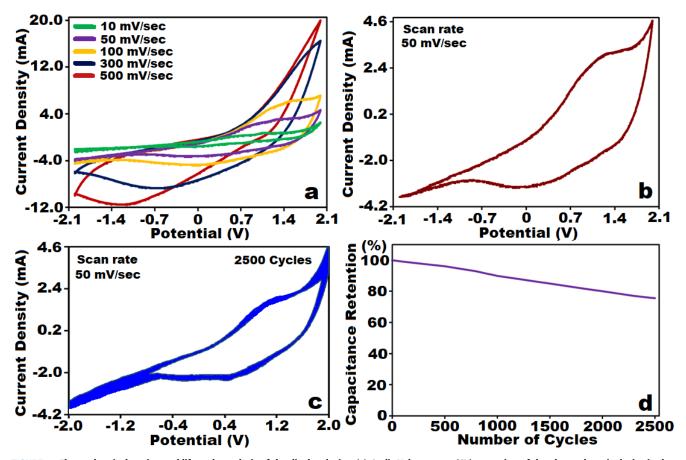


FIGURE 4. Electrochemical testing and life cycle analysis of the display device. (a) Cyclic Voltammetry (CV) operation of the electrochromic device in the range of -2.0 to +2.0 V with the scan rate of 10 mV/sec to 500 mV/sec. (b) CV analysis on 50mV/sec scan rate for electrochromic device. (c) Stability analysis by performing 2500 cycles of CV analysis at 50mV/sec scan rate. (d) Stability investigation by plotting the specific capacitance retention percentage over the number of cycles.

been also observed that the specific capacitance value of the device decreases, at the same time the reversible color (electrochromism) property of the device also decreases. We found that the specific capacitance retention property is also indicating the electrochromic device stability.

It is concluded, that this three-layer very compact device is very stable since it can maintain its electrochromic property at least 2500 cycles of the run, whereas this device follows crude handmade fabrication. The device can retain more than 75 % of specific capacitance efficacy, or in other words electrochromism efficacy even after 2500 cycles of the run. It also has been observed that if the voltage is increased to -2.5 V to 2.5 V after the 2500<sup>th</sup> cycle, the device can regain the 100% electrochromism but the life became shorter because of the gel-based phosphoric acid electrolyte.

The assembled electrochromic device is highly flexible; it performs quite normal even the device is completely folded or bent (Figure 1c and d). Yet, the bending stability of the electrochromic device has been investigated over 1500 times bending. Figure 5a shows the lab-made bending apparatus, which is a hydraulic based instrument with the bending speed ranging from 0.5 turns/sec to 10 turns/sec. The vigorous bending experiment was performed in two different ways.

In the first method, primarily bending has been performed and then the electrochromic device has been assembled, whereas in the second method, at the first electrochromic device has been assembled then bending has been performed afterword. For both the procedures, the 2 turns/sec bending speed has been accumulated. There were three samples of the electrochromic electrode has been taken for the first method as control (without bent), 1000 times bent, and third 1500 times bent. Afterward, the electrochromic device has been manufactured of all the three different samples in similar and the same size. The performances were investigated with the help of the Zive SP1 Electrochemical work station by providing  $\pm 2.0$  V supply to all the three samples one by one. Figure 5b shows the bending resultants of this method, it can be observed that there are no observable discriminative defects in dark blue color variations (oxidation) in 1500 times bent or 1000 times bent electrode electrochromic device over without bent electrode electrochromic device. Yet, there were some observable kinks appear because of the repetitive vigorous rough folding in 1500 times bent and 1000 times bent electrode electrochromic devices.

Despite these random kinks, all three samples (control, 1000 times bent and 1500 times bent) were having



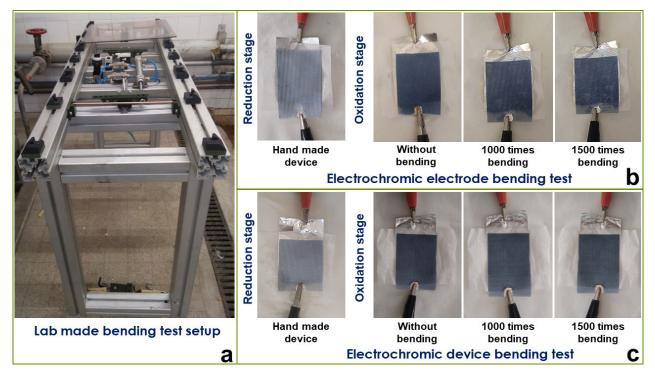


FIGURE 5. Bending setup and bending effect on electrochromic behavior. (a) Lab-made bending set up with the speed of 2 turns/sec. (b) Electrochromic property variation comparison over control (without bending), 1000 bending and 15000 bending in first method (electrochromic electrode bending then device making). (c) Electrochromic property variation comparison over Control (without bending), 1000 bending and 15000 bending in second method (first electrochromic electrode device fabrication then bending).

almost identical electrochromic effects, and the switching time was similar too.

The second method is quite different over the first method, as in this technique single electrochromic device is used for all the bending experiments rather than three different electrochromic devices. For the second method, an electrochromic device has been fabricated and performed electrochromic testing. The same device has been bent for 1000 times and recorded its electrochromic performance, furthermore, this electrochromic device has been bent for 500 times more (total 1500 times) and investigated its electrochromic performance. It has been observed that there were no identifiable electrochromic defects found even after 1500 times bending (Figure 5c). Similar to the first method, there were also some minute kinks seen in this bending process, but they were not so prominent. Thus, Thus in this second method also electrochromic devices performed almost similar in all respect (even in terms of switching time) even after 1500 times or 1000 times bandings. Hence, it can be concluded, as there were no observable electrochromic defects found even after 1500 times of bending in both methods of bending test. Although in appearance, there is no observable impact on the designed compact electrochromic device by the vigorous bending process, yet, it is also important to investigate the electrochemical changes over 1500 times bending. The CV analysis has been performed for both the different methods of bending by using the Zive SP1 Electrochemical work station over the  $\pm 2.0$  V power supply. Figure 6a shows the comparative CV analysis of control (without bent),

1000 times bent and 1500 times bent electrochromic device by following the first method approach (electrochromic electrode bending then device making). It can be observed that either 1000 times bent or 1500 times bent CV, both are following the same oxidation or reduction peaks as in control CV. It shows that there was no electrochemical imbalance happened because of the bending. The current density and specific capacitance for the 1000 times bent and 1500 times CV is almost the same, it means there was no degradation in electrochromic behavior (because of identical charging and discharging currents) of electrode bending electrochromic device from 1000 times bending to 1500 times bending. Yet, there is some specific capacitance, anodic and cathodic current decrement can be observed between control CV and 1500 times/1000 times bent CV. It may be happening because of the ohmic loss (equivalent series resistance) and sluggish kinetics of electrochemical activities happened because of bending. There could be some contact areas in the electrochromic device where irregularity came across after banding, which creates the extra ohmic loss and insufficiency in ions diffusion. This is happening because the crude electrochromic device was fabricated in the lab by hand. However, the automatized fabrication of this electrochromic device can properly avoid these losses. Similar effects can be seen in the second method (first electrochromic electrode device fabrication then bending) CV too (Figure 6b).

It can be seen in Figure 6b that the oxidation and reduction peaks for 1500/1000 times bent devices CV are almost similar to control CV. Similar to the first method approach there is

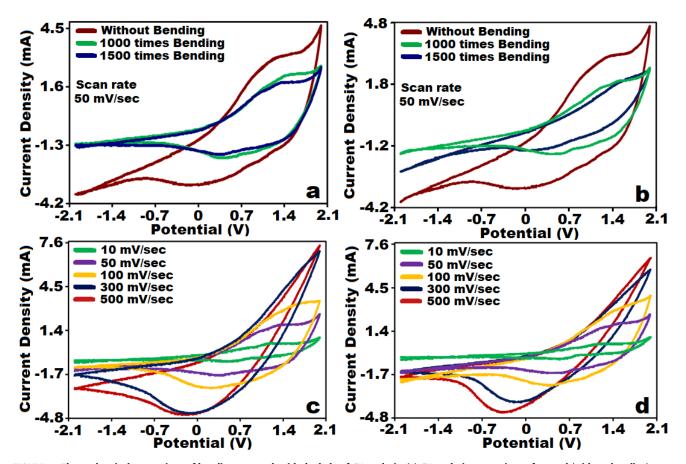


FIGURE 6. Electrochemical comparison of bending approach with the help of CV analysis. (a) CV analysis comparison of control (without bending), 1000 bending, and 15000 bendings in the first method approach. (b) CV analysis comparison of Control (without bending), 1000 bending and 15000 bending in the second method approach. (c) CV analysis at different scan rates ranging from 10mV/sec to 500mV/sec for the first bending method approach. (d) CV analysis at different scan rates ranging from 10mV/sec for the second bending method approach.

a difference in the anodic and cathodic current density, and specific capacitance in 1500 bends and 1000 bends CV over control CV. The reason is quite similar as explained in the first method approach.

Furthermore, we have also performed CV analysis at different scan rates for 1500 times bent device for both methods approach to observe its stability. Figure 6c shows the CV analysis at different scan rates ranging from 10mV/sec to 500mV/sec in the voltage range of -2.0 V to +2.0 V for the first method approach and Figure 6d shows the same for the second method approach. It can be observed that the CV analysis for 1500 times of bent device (Figure 6c and d) for both the method are similar to control (without bending device) CV analysis (Figure 4a) except peak anodic and cathodic current density. As it has been explained that this might be happened because of the improper fabrication because of the handmade process, when the fabrication system will automatize, this will be also dissolved. So, it can be concluded as even after 1500 times of folding, the lab-made crude electrochromic device is very well functional with a slight variation in electrochromic efficacy. This signifies the extreme flexibility of the designed electrochromic device.

The designed electrochromic device is having just three-layer with thin 140 dtex polyester-based fabric, a thin biocompatible gel electrolyte H<sub>3</sub>PO<sub>4</sub> layer (0.2mm), and a thin 0.001in aluminum sheet, which signifies its compactness. The used materials are polyester fabric, 1 M phosphoric acid, aluminum sheet, tissue paper (semi-permeable membrane), and PEDOT:PSS, these all materials are biocompatible and robust so the fabricated device is biocompatible and highly robust. Besides, all these materials are very economical, the fabrication process is very straightforward and convenient, and need just 2.0 V supply, which signifies its cost-effectiveness and efficiency. Overall, the designed electrochromic device is compact, biocompatible, highly flexible, stable, robust, efficient, and economical.

In the future, we are aiming to make a seven-segment display for an automatic car dashboard. Instead of this context, all analyses (even stability) by two segments display were performed.

In Supplementary video 3 (also in supplementary video 4), the two similar electrochromic devices have been connected to the Zive SP1 Electrochemical work station for two segment



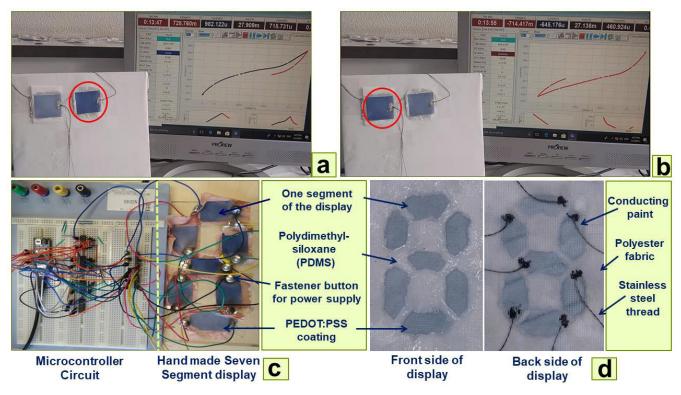


FIGURE 7. Two-segment display analysis and future aspects of the seven-segment display. (a) Two segment display analyses with CV while -2.0 V to +2.0 V run of the cycle, and observation in the color change in the left segment. (b) +2.0 V to -2.0 V run of CV cycle and the color change in the right segment. (c) Microcontroller circuit-based hand-made seven-segment display. (d) Single fabric seven-segment display.

display operations synchronized with CV analysis. For this synchronized operation observation, the power supply connections of both devices were opposite to each other (if one electrode of the first device is connected to the positive terminal then a similar electrode of the second device is connected to the negative terminal) and in respect of that, both segments would display opposite colors in a synchronized manner with the CV. A CV analysis has been applied through the user interface of the electrochemical work station in the voltage range of -2.0 V to +2.0 V and the scan rate was 100 mV/secin supplementary video 3 (300 mV/sec for supplementary video 4). Figures 7a and 7b are a snapshot of the functioning video of the two-segment display in a synchronized way with CV analysis. In supplementary videos 3 & 4, when +2.0 V to -2.0 V CV runs, the right-side segment displays the color change from light grey to dark blue (reduces) and the left side segment displays color disappearance from dark blue to light grey (oxidized) in Figure 7a. On the opposite cycle of the run, when scanning performs from -2.0 V to +2.0 Vthe left side segment shows the color change from light grey to dark blue due to reduction and the right side segment shows color disappearance from dark blue to a light grey due to the oxidation (Figure 7b) and this continues until the CV runs. It can be observed that the two-segment display is performing very well and synchronized with the CV scan rate, which signifies that this three-layer efficient textile-based electrochromic device can perform well for future dashboard display.

The seven-segment display was also fabricated in a similar process as the two-segment display was formed, it means incorporating one device by one individual segment and controlled by a microcontroller circuit board (Figure 7c). On a positive note, the operation of the seven-segment display was observed by this arrangement, but due to the number of wired connections complexity of these seven similar devices, the controlling and fixation was very difficult. As result, this seven-segment display was not very stable. Therefore, we are trying to make a seven-segment display in a single fabric (Figure 7d). With the incorporation of polydimethylsiloxane (PDMS), we can provide the shape of each segment. By using conducting paint and stainless-steel thread the supply to each separate segment will be provided. In the future, this seven-segment display will come into existence.

The current electrochromic device is tested at room conditions. In the future, this device will be tested and modify accordingly for extreme conditions of temperature, humidity, and sunlight. There is one more concern is the washability of PEDOT:PSS based electrochromic device. Yet, the coating of the silicon layer on the top of the electrochromic device is one the best solution to improve washability but, it needs more in-depth research to improve washability. This will be also a future goal of this work.

### **IV. CONCLUSION**

This article gives a new face to electrochromic display research. The developed electrochromic device is having only



a three-layer structure with the textile substrate. The materials which are used to fabricate the electrochromic device is supporting the biocompatible aspects. Different fabrics and dilution ratios of PEDOT:PSS solutions have been tested. The readymade 140 dtex polyester flex printing-based textile fabric directly coated by 2.0 times ratio diluted PEDOT:PSS solutions was performed the best for the two-segment electrochromic display. Our simple structured display device is having a very high life cycle as it can run up to 2500 cycles without degradation. It is highly flexible and robust as it can function properly even after 1500 times of banding. Therefore, in the quest for automatization in the automobile interiors, this device can provide big support as it is a very flexible, robust, optimized structured, economical, biocompatible, very high cycle life, fast switching, and run at very low voltage (2.0 V). Currently, it has been added with a microcontroller circuit to observe the switching behavior for two similar devices.

The broader future goal of this research is to design the driverless automobiles interior display and especially dash-board display. The possible solutions are electrochromism through hybrid fabrics (especially with optical fibers), embroidery and jacquard weaving (for seven segment display), and many more. So, taking this future goal in the view, we have performed the yarn coating process that is also our second alternative of making an electrochromic displaying electrode.

#### **REFERENCES**

- A. Kubacka and M. Fernández-García, "Chromism and catalysis shake hands," *Nature Catal.*, vol. 1, no. 9, pp. 643–644, Sep. 2018, doi: 10.1038/ s41929-018-0151-0.
- [2] C. Granqvist, "Out of a niche," *Nature Mater.*, vol. 5, no. 353, pp. 89–90, 2006, doi: 10.1038/nmat1577.
- [3] G. Sonmez, H. B. Sonmez, C. K. F. Shen, and F. Wudl, "Red, green, and blue colors in polymeric electrochromics," *Adv. Mater.*, vol. 16, no. 21, pp. 1905–1908, Nov. 2004, doi: 10.1002/adma.200400546.
- [4] R.-T. Wen, C. G. Granqvist, and G. A. Niklasson, "Eliminating degradation and uncovering ion-trapping dynamics in electrochromic WO3 thin films," *Nature Mater.*, vol. 14, no. 10, pp. 996–1001, Oct. 2015, doi: 10. 1038/nmat4368.
- [5] F. M. Kelly, L. Meunier, C. Cochrane, and V. Koncar, "Polyaniline: Application as solid state electrochromic in a flexible textile display," *Displays*, vol. 34, no. 1, pp. 1–7, Jan. 2013.
- [6] C. M. Amb, A. L. Dyer, and J. R. Reynolds, "Navigating the color palette of solution-processable electrochromic polymers," *Chem. Mater.*, vol. 23, no. 3, pp. 397–415, Feb. 2011.
- [7] A. W. Lang, Y. Li, M. D. Keersmaecker, D. E. Shen, A. M. Österholm, L. Berglund, and J. R. Reynolds, "Transparent wood smart windows: Polymer electrochromic devices based on Poly(3,4-Ethylenedioxythiophene):Poly(styrene sulfonate) electrodes," ChemSusChem, vol. 11, no. 5, pp. 854–863, 2018.
- [8] H. W. Heuer, R. Wehrmann, and S. Kirchmeyer, "Electrochromic window based on conducting Poly(3,4-ethylenedioxythiophene)-Poly(styrene sulfonate)," Adv. Funct. Mater., vol. 12, no. 2, pp. 89–94, Feb. 2002.
- [9] D. Levasseur, I. Mjejri, T. Rolland, and A. Rougier, "Color tuning by oxide addition in PEDOT: PSS-based electrochromic devices," *Polymers*, vol. 11, no. 1, pp. 179–191, 2019.
- [10] F. M. Kelly, L. Meunier, C. Cochrane, and V. Koncar, "A flexible electrochromic display using solid or liquid phase conducting polymers," in *Proc. 12th World Textile Conf.*, 2012 pp. 1405–1410.

- [11] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J. R. Reynolds, "Poly(3,4?ethylenedioxythiophene) and its derivatives: Past, present, and future," Adv. Mater., vol. 12, no. 7, pp. 481–494, 2000.
- [12] Y. Xia and J. Ouyang, "Significant conductivity enhancement of conductive Poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate) films through a treatment with organic carboxylic acids and inorganic acids," ACS Appl. Mater. Interface, vol. 2, no. 2, pp. 474–483, Feb. 2010.
- [13] J. Ouyang, C.-W. Chu, F.-C. Chen, Q. Xu, and Y. Yang, "High-conductivity Poly(3,4-ethylenedioxythiophene):Poly(styrene sulfonate) film and its application in polymer optoelectronic devices," *Adv. Funct. Mater.*, vol. 15, no. 2, pp. 203–208, Feb. 2005, doi: 10.1002/adfm.200400016.
- [14] L. Meunier, F. M. Kelly, C. Cochrane, and V. Koncar, "Flexible displays for smart clothing: Part II—Electrochromic displays," *Indian J. Fibre Text. Res.*, vol. 36, pp. 429–435, Dec. 2011.
- [15] D. Mecerreyes, R. Marcilla, E. Ochoteco, H. Grande, J. A. Pomposo, R. Vergaz, and J. M. S. Pena, "A simplified all-polymer flexible electrochromic device," *Electrochim. Acta*, vol. 49, no. 21, pp. 3555–3559, Sep. 2004.
- [16] F. M. Kelly, L. Meunier, C. Cochrane, and V. Koncar, "Evaluation of solid or liquid phase conducting polymers within a flexible textile electrochromic device," *J. Display Technol.*, vol. 9, no. 8, pp. 626–631, Aug. 2013.
- [17] A. Dubey, S. K. B. Singh Tulachan, M. Roy, G. Shrivastava, D. Philip, S. Sarakar, and M. Das, "Nano iron pyrite (FeS<sub>2</sub>) exhibits bi-functional electrode character," *RSC Adv.*, vol. 6, no. 20, pp. 16859–16867, 2016, doi: 10.1039/C6RA01973K.
- [18] A. Dubey, H. Jangir, S. Verma, M. Saxena, S. Sarkar, D. Philip, and M. Das, "Biocharring of natural fibers of insect and plant origin: A green route for the production of 'carbon-based charge storage nanomaterials," *Mater. Renew. Sustain. Energy*, vol. 7, no. 4, p. 20, Nov. 2018, doi: 10.1007/ s40243-018-0127-7.
- [19] A. Dubey, H. Jangir, M. Pandey, M. M. Dubey, S. Verma, M. Roy, S. K. Singh, D. Philip, S. Sarkar, and M. Das, "An eco-friendly, low-power charge storage device from bio-tolerable nano cerium oxide electrodes for bioelectrical and biomedical applications," *Biomed. Phys. Eng. Express*, vol. 4, no. 2, Feb. 2018, Art. no. 025041, doi: 10.1088/2057-1976/aaa282.

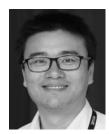


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