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**Development of Screen Printed, PEDOT:PSS Based, a
Stretchable Electrochromic Device with a Solid-State
Electrolyte**

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Abbreviations

EDOT	3,4-ethylene dioxythiophene
EG	ethylene glycol
ITO	indium tin oxide
OECT	organic electrochemical transistor
OLED	organic light-emitting diode
PEDOT	poly(3,4-ethylene dioxythiophene)
PET	poly(ethylene terephthalate)
PSS	polystyrene sulfonate
PU	polyurethane
PVA	poly(vinyl alcohol)
WbPUD	waterborne polyurethane dispersion

1. Introduction

Electrochromism is a material phenomenon when it undergoes a color change due to electron transfer upon applied electrochemical potential. Electrochromic pixels can be a low-cost alternative for conventional displays due to inexpensive materials, energy efficiency, and facile fabrication processes. In contrast to their inorganic counterparts, polymeric electrochromic materials have much lower elastic moduli and, therefore, could be used for the development of stretchable electronics using scalable fabrication techniques, such as screen printing or roll-to-roll printing. Screen printing technology allows to create thin films cost-effectively and simply at a sufficiently high spatial resolution while retaining the capability of the rapid prototyping process. Electrochromic devices can be cheaper, energy-efficient alternatives to various screen-like devices. However, a stretchable polymer-based electrochromic device must be created beforehand to create a stretchable screen-like device.

This work aims to create a prototype of the stretchable, printable electrochromic device using poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT:PSS) as the electrochromic material. To achieve this goal, three main tasks were established:

- Create a printable and stretchable composite based on PEDOT:PSS that can be deposited using print technology. Optimize the composition of the material and characterize it.
- Design a solid, stretchable, transparent polymer-based electrolyte that could join with PEDOT:PSS electrochromic composite preventing phase separation between the two.
- Design an electrochromic device based on the created PEDOT:PSS electrochromic composite and polymer-based solid electrolyte and fabricate a working prototype of this device.

2. Literature review

2.1. Organic electronics

Organic electronics are based on organic and polymeric materials that possess conducting and semiconductors-like properties similar to inorganic counterparts while having a lot of advantages, such as potentially low cost, energy efficiency, and high mechanical flexibility, to name a few. Technology based on organic electronics outperforms and replaces inorganic devices in several applications [1]. Organic semiconductors, on which many organic electronics are based, are similar to silicon-based semiconductors. However, they are composed of carbon, hydrogen, and other lightweight elements. Additionally, organic molecules and polymers can be easily modified through chemical synthesis, and thus, their properties can be effortlessly tailored to suit the desired application. This makes organic electronics perfect to represent the future of electronics [1].

One of the examples can be organic light-emitting diodes (OLEDs), they are already widely used and implemented in everyday technology, and they are shown to be more energy efficient [2]. Another heavily researched example of organic electronics is the organic electrochemical transistor (OECT). A working principle is similar to a conventional transistor that can be switched on and off by applying a potential to the gate. However, the structure and the working principle are vastly different. In the organic electrochemical transistor, the organic semiconductor, PEDOT:PSS (poly(3,4-ethylene dioxythiophene) polystyrene sulfonate), is connected to two electrodes, the source and drain, which move charges in the channel. And the gate electrode is connected to the electrolyte. If sufficient potential is applied to the gate electrode, ions are pushed from the electrolyte to the organic semiconductor, changing its redox state and altering materials conductivity. OECTs operate solely based on electrochemical principles. The most established semiconducting material for OECTs is previously mentioned PEDOT:PSS, a p-type semiconductor – PEDOT, doped by PSS [1,3,4].

Due to not using any rigid materials in the fabrication of the OECT, completely flexible or even stretchable transistors can be created [3,5]. The switching speed of the PEDOT:PSS-based OECT can be up hundreds of times per second. Unfortunately, the switching rate should be much faster for a real-life computational device. However, the novel working principle of the OECT allows it to potentially be used as a fundamental building block to create a genuinely neuromorphic device. Devices like these can create a new generation of not-silicon based artificial intelligence. This advancement in technology will require significant effort and interdisciplinary collaboration. This illustrates the example that organic electronics can be used differently from conventional electronics, creating unusual and unique applications. This is one of the reasons why it is essential to investigate and research organic electronics [5–7].

2.2. Electrochromic devices

Electrochromism is a process when the absorbance of the material changes if an electrochemical potential is applied. The color changes reversibly and fades away slowly when applied potential is removed. The significance of electrochromic technology is growing because it is associated with energy conservation and energy-efficient displays. Electrochromic devices are made of several thin layers:

- electrochromic layer (organic, polymeric, or inorganic),
- an ionic electrolyte (solid or liquid/ Li^+ , H^+),
- an ion storage layer,
- and a transparent electrode [8–10].

When a potential is applied, the ions move into the electrochromic layer resulting in doping/de-doping (reduction/oxidation) and thus color change.

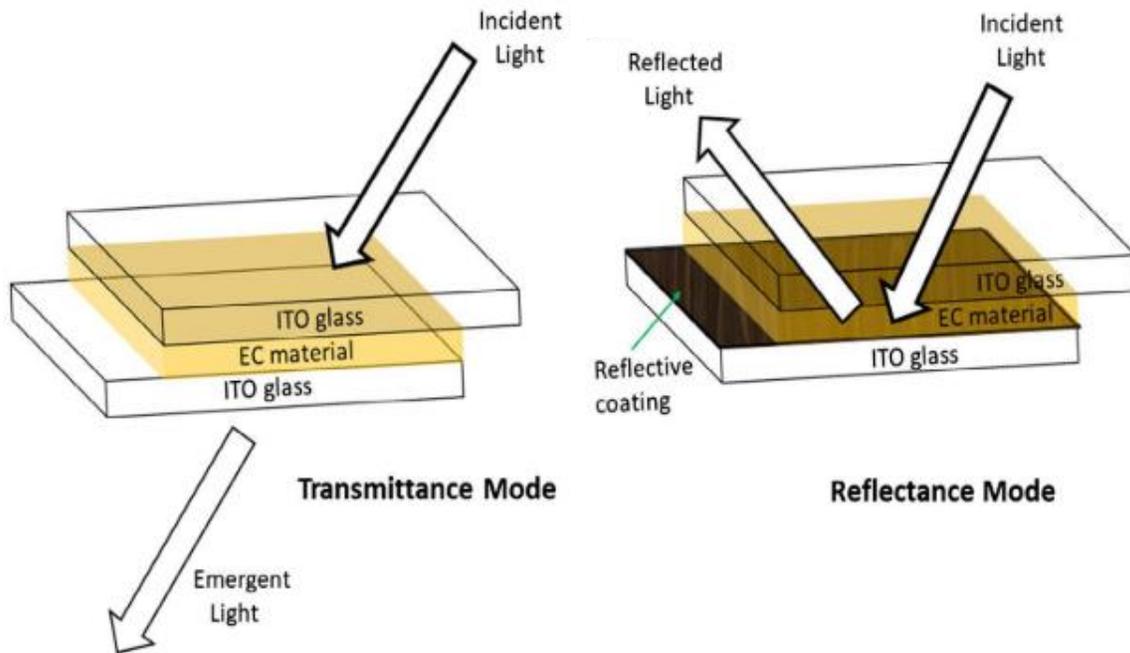


Figure 1. Modes of electrochromic device operation: transmittance mode(left) and reflectance mode (right) [8].

There are a few types of electrochromic devices: operating in a transmittance mode or reflectance mode (Figure 1). Reflectance mode operates by reflecting light using reflective coating below electrochromic material, for example, used in rearview mirrors. In devices that work in transmittance mode, light passes through the device. Thus, the device, such as smart windows or smart glasses, must be entirely constructed from transparent materials [8].

Ideally, the electrolyte used in fabrication of electrochromic devices must be transparent, solid, have a wide electrochemical window and exhibit remarkably high conductivity. This is necessary to achieve fast switching of the device. It is possible to simplify the structure of the electrochromic device by removing the ion storage layer and adding one more layer of the electrochromic material (PEDOT:PSS), resulting in the symmetric device [10,11]. During this work, the primary focus will be on electrochromic material and solid electrolytes that will be used to fabricate prototype of electrochromic device operating in transmittance mode. Other parts of the electrochromic device might be optimized and developed in the future.

2.2.1. Characteristics of electrochromic devices

Electrochromic contrast, coloration efficiency, write-erase efficiency, switching speed, stability, cycle life, and optical memory – are the parameters that are necessary to optimize before electrochromic material and electrochromic devices can be considered for potential applications. The electrochromic contrast or contrast ratio is a quantitative parameter that describes ratio between transmittance of the electrochromic material in its bleached state and the transmittance in the colored state. The coloration efficiency shows the ratio of the absorbance change to the charge carriers injected per electrode area. Optical memory is a parameter that describes how long the device can stay in its colored/bleached state after the voltage is removed. For practical purposes, electrochromic devices should not degrade or lose their performance for at least ten thousand switches [12–14].

2.2.2. Electrochromic polymers

Even though there are several types of electrochromic materials, such as:

- inorganic electrochromic material (Prussian blue, metal oxides (WO_3)),
- metal-organic electrochromic materials (metal phthalocyanines),
- small organic molecules (viologens),
- conjugated polymers (polyaniline),

however, in this work, only polymers will be discussed. Electrochromic polymers are known for being easily processable, their color can be adjusted through copolymerization or chemical synthesis, and usually, they are cheaper than alternatives. Additionally, they have a long lifetime, high optical contrast, stable oxidation states, excellent switching reproducibility, and, most important, flexibility. They have semi-bistability, which allows one to retain color even when disconnected from the source for several hours. Due to their flexibility, they can be applied to uneven surfaces or even in stretchable devices. Some polymers have more than two stable oxidation states, allowing multiple color systems [15]. These advantages are why electrochromic polymers are already finding application in displays, smart windows, sunglasses, and smart paper.

They are expected soon to be used in camouflage materials, controllable display devices, and smart textiles [16–19].

While working with electrochromic polymers, the main concerns are challenging synthesis processes, low thermal stability, slower than inorganic material switching time, and lack of mechanical properties. Some of these issues can be solved by changing the molecular structure and inserting electroactive moieties into the polymer backbone to enhance the optical and mechanical properties of the electrochromic material [15].

Conjugated and electroactive polymers can be created using aromatic ring systems, including aniline, pyrroles, and thiophenes. These conductive polymers have found applications in a range of areas, e.g., sensors and organic light-emitting diodes, photovoltaics, and lasers [20–22]. Because conjugated polymers can be oxidized or reduced between two optically and electrically distinct states, they can be used as electrochromic thin films. Electroactive conducting polymers offer the following advantages over inorganic compounds:

- outstanding coloration efficiency
- energy efficient
- multiple colors from the same material
- fine-tuning of bandgap by chemical modification [11,13,15]

The films of polyaniline formed by cyclic potentiostatic polymerization of aniline in an aqueous HCl solution are much studied [17,18]. Polyaniline can exist in four different redox states, with the historical names of leucoemeraldine, emeraldine salt, emeraldine base, and pernigraniline. Electrode films of polyanilines are therefore multi-colored and show color changes from the yellow form and from dark blue to black, depending on the potential.

2.2.3. PEDOT:PSS

Other essential electrochromic polymers are the polypyrroles and polythiophenes, obtained by chemical or electrochemical polymerization of the monomer, pyrrole and thiophene or, more importantly, their 3,4-disubstituted derivatives. The polythiophenes are the most widely studied of these two classes of polymers in electrochromic outlets. The synthesis and development of a variety of electroconductive polymers were greatly assisted when the monomer 3,4(ethylenedioxy)thiophene (EDOT) and the derived polymer PEDOT became commercially available, especially as a water-soluble complex (PEDOT:PSS) with the polyelectrolyte poly(styrene sulfonate) [23]. PEDOT is blue in the neutral state and transmissive sky blue in the oxidized state. Hence, this can be used to create color-changing electrodes and electrochromic devices (Figure 2). This is extremely useful because PEDOT:PSS can be used as conducting and electrochromic material, thus reducing the number of elements in an electrochromic device. PEDOT:PSS is a highly attractive material for a broad range of applications, including fuel cells, supercapacitors, transistors, and electrochromic devices, as in this work. Using pyrrole derivatives, modified EDOT monomers and related structures, it is possible to make donor-acceptor polymers

showing a spectrum of colors from yellow through red to blue in the neutral state [11,24]. Hence, varying the structural elements in such polymers to achieve stable materials having a full-color spectrum has been an extensive area for research in the last 10–15 years [25–27].

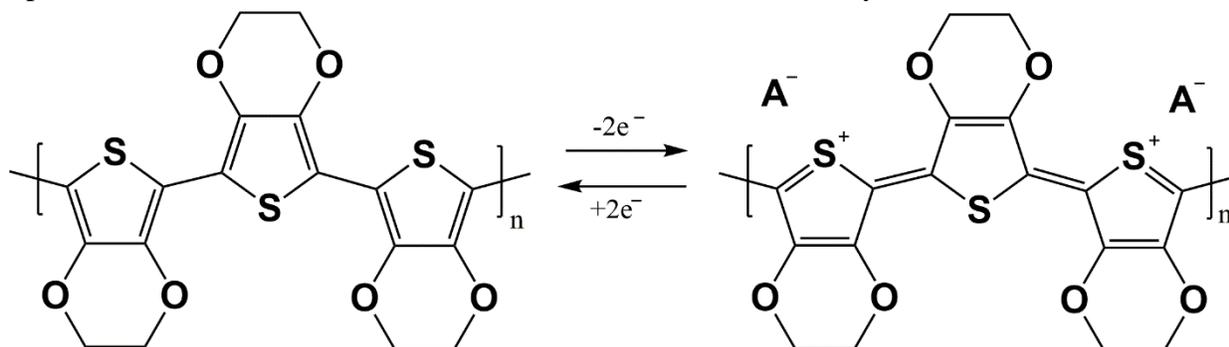


Figure 2. Reduction and oxidation of PEDOT. Reduced state has a dark blue color (left). Oxidized state, PEDOT⁺, is transparent blue and positive charge is compensated by negative particles (A=PSS⁻).

To allow for the solution processing of PEDOT, insulating poly(styrene sulfonic acid) (PSS) is added to PEDOT, making it semi-soluble in water. However, the electrical conductivity of PEDOT:PSS can further be tailored by the addition of additives such as **ethylene glycol**, tetramethylene sulfone, and dimethyl sulfoxide [28,29]. These approaches make PEDOT:PSS a promising material for a wide variety of applications: electrochromic textile, elastic displays, and solar cells, to mention a few. Commonly, PEDOT:PSS films are deposited using spin coating for photovoltaic and optoelectronic devices. However, these methods are not optimal for industrial use because they are hard to scale. Emphasis on large-area printed electronic devices has led to various roll-to-roll processing techniques such as screen printing and inkjet printing to print PEDOT:PSS films [30]. While in the past, screen printing has been used extensively for silver inks as a back electrode in solar cell fabrication, scientists have used the screen-printing technique for the deposition of PEDOT:PSS in the fabrication of large-area polymer-based solar cells.

The commercially available PEDOT:PSS aqueous dispersion is a deep blue opaque solution. It can form a continuous thin film on either rigid or flexible substrates by different solution processing methods, including spin coating, spray deposition, inkjet printing, and screen printing. The PEDOT:PSS film is smooth and has a surface roughness less than 5 nm (deposition technique dependent). PEDOT:PSS film is highly translucent in the visible light range; a 100 nm thick layer can exhibit a transmittance (T) above 90 % at 550 nm. PEDOT:PSS displays a wide range of electrical conductivities from 10^2 to 10^3 S/cm, influenced by synthesis conditions, processing additives, or post-treatment [27,29,31]. The high conductivity and great work function can frequently generate spontaneous charge transfer with fast kinetics, thus presenting PEDOT:PSS with catalytic properties. PEDOT:PSS has great photo and electrical stability in air, is physically and chemically stable in ambient atmosphere.

PEDOT:PSS in its neutral state consists of PEDOT⁺ and PSS⁻. When potential is applied it is possible for the cations (Li⁺, H⁺) from the electrolyte to be inserted and rearranged in the

PEDOT:PSS structure. Then, positive charge compensates for the negative charge of the PSS⁻ and this results in reduction of PEDOT⁺ to PEDOT⁰. This can be depicted as:



When PEDOT is reduced it becomes dark blue color and during the oxidation it becomes almost transparent. If thin enough layer of PEDOT:PSS is deposited it can be almost colorless and transparent being great alternative for high performance transparent electrodes such as made from ITO. Even though scientists are researching PEDOT:PSS for a long time and it has a lot of applications, exact mechanism of ion transport is not completely explained. This is because PEDOT:PSS has mixed conductivity, which complicates experimental methods to examine this [32].

One of the complications when creating stretchable devices with PEDOT:PSS is lack of internal stretchability. Dry and pristine PEDOT:PSS films are highly brittle and hard; Youngs modulus is 10⁶ Pa and PEDOT:PSS breaks at strain higher than 6 %. Several types of additives can be added to overcome this problem including ionic liquids, fluorosurfactants or polymers (PEG or PVA). Alternatively, it is possible to synthesis copolymers that possess desired characteristics. These approaches successfully lower Youngs modulus and make it more stretchable [33–36].

2.3. Printed electronics

Printed electronics describe a type of devices that are produced using printing technology. Electronic circuits, sensors, transistors, displays can be printed and based on organic semiconductors as well as printable inorganic substances (Figure 3). It can provide new functionality to things used daily, for example, smart clothes or smart food packaging.



Figure 3. PEDOT:PSS based fully printed stretchble double seven segment display. Deposited onto textile and displaying number 26 (left), display compeletly adhearing to round suraface due to its stretchability (right) [20].

Most importantly, technology based on printed electronics emerged as a low-cost replacement to the conventional electronics, however now more advantages can be seen: uncomplicated process, that are less time consuming, less material waste is produced. Printing technology is extremally efficient in producing components aiming at high-volume market

segments where the high performance of conventional electronics is not required [37]. Printing techniques utilized to create printed electronics are flexographic, offset, screen, and inkjet printing, each having its benefits and limitations [38].

2.3.1. Screen printing

Screen printing technology is a mature technology, and there are five main components: a stencil with mesh, a squeegee, functional ink, a screen printer stage, and a substrate [39]. Some of the elements used in screen printing technology are shown in Figure 4.

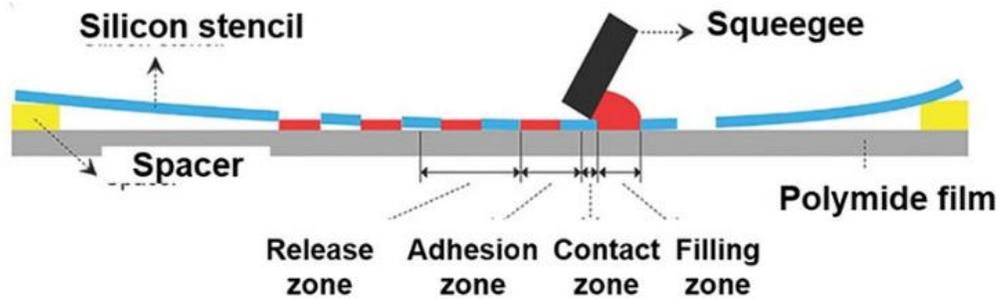


Figure 4. Cross-sectional illustration of the screen-printing method to deposit ink [5].

As shown in Figure 5, the procedure of screen-printing involves two main steps. The first step is the incursion of ink through the mesh in the stencil, and the second is deposition onto the substrate and forming the requisite patterned electrodes [40]. Due to the flexibility of PET, paper, and textile as substrates, bendable or even stretchable electronics can be printed [41].

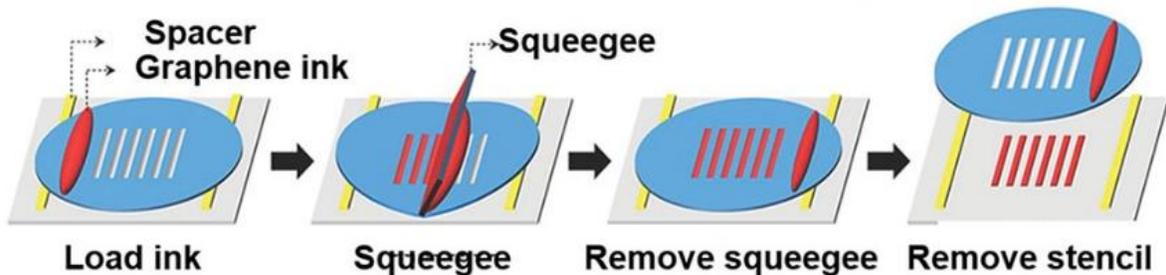


Figure 5. The image presents manufacture process of electrodes with screen-printing technology and graphene ink [5].

Patterned electrodes and circuits can transfer shapes accurately with the opening. Benefiting from a straightforward procedure, the viability of mass production, adjustable patterns, and low-cost, screen-printing technology is one of the most popular methods to fabricate electrodes on flexible substrates up to date. One additional advantage of this method is that it is easily scalable and can be used in the industrial manufacturing of stretchable electronics [41]. Just like the traditional method of fabricating electrodes, screen-printing technology also falls under the top-down approach. Due to the weak connection among the ink and the substrate, the viscosity and

squeegee perform a key role in the solution. They must be addressed during the development of ink [30].

2.3.2. Screen printed stretchable electrochromic displays

Wearable and soft technology and electronics are crucial advancements before creating affordable, intelligent, and personalized technology that can be used in smart clothes or skin patches. The necessity of the visual interface for the user makes a screen-like device crucial for this type of advancement. For the screen-like device to be securely fixed to the surface without discomfort for the wearer, it must be soft, easily adjustable, and stretchable while not losing its functionality [20,42,43]. A few types of developed technologies can be used as a display in a stretchable device. A stretchable circuit board can be used with mounted OLEDs. Stretchable light-emitting electrochemical cells are being developed, and alternative stretchable electroluminescent displays are considered for this application. Their bulky design and need for high voltages to operate limits their application in wearable electronics [38,44]. This creates the necessity for cheap, simple, energy-efficient technology that can be used instead. Appealing technology to be used instead is previously mentioned electrochromic displays. Electrochromic cells (pixels) usually range from few millimeters up to decimeters in size, this makes screen-printing great method to manufacture it. Just like other additive manufacturing techniques, screen printing produces minimal amount of waste. Unlike photolithography, which can be used to produce patterns with much higher resolution, resolution of screen-printing is around few millimeters, but it does not require any particular conditions, such as yellow light room or vacuum chambers. Additionally, screen printing can be done onto various substrates: PET, thermoplastic polyurethane, textile or paper [22,45–47].

2.4. Solid electrolyte

Solid-state electrolytes are being thoroughly researched due to the emergence of high-performance materials, novel applications, and safety concerns and are being used in electrical energy storage in batteries. Solid-state electrolytes are much safer than liquid electrolytes because the risk of leakage is removed. This is crucial for wearable devices, where safety is a number one priority. Two types of solid-state electrolytes are now being developed and researched: solid inorganic electrolytes and solid polymeric electrolytes [48].

Even though solid inorganic electrolytes have plenty of advantages: high ionic conductivity (>0.1 mS/cm at room temperature), high moduli (>1 GPa), large electrochemical stability window (>4.0 V), and high thermal stability (>100 °C), there are concerning issues that prevent them from being used commercially. Solid inorganic electrolytes are fragile in large areas, thus making them difficult to manufacture, excessive cost, low environmental stability, risk of growing dendrites, and comparably faulty contact with electrodes resulting in slow charge

transport at the interface. There are efforts to solve these issues; however not entirely successful [49].

When comparing inorganic and polymeric solid electrolytes, it becomes apparent that polymer-based electrolytes are much cheaper to produce, easily synthesized, more resilient to environmental factors, can be easily scaled for mass production, and can be modified by chemical synthesis, copolymerization, or crosslinking. Unlike inorganic materials, the polymeric solid electrolyte can be elastic and soft, making them great for wearable electronics. Unfortunately, polymer solid electrolytes have lower conductivity, and dielectric constant and polymer crystal lattice can prevent cations from moving freely.

Since polymer and inorganic solid electrolytes have very distinct advantages, one can see how these materials can be used together to create composites and combine the best of both worlds. One of the earliest efforts to combine these two types of material was adding inorganic fillers that improve mechanical strength and thermal stability and induce the formation of amorphous poly(ethylene oxide) [49].

Few aspects must be considered to prepare and perfect polymer solid electrolytes. The concentration of salts should be optimized. If the dissolved salt concentration is low, increase of it will add charge carriers, thus increasing conductivity. However, when the concentration of the salts is too high, polymer salt crystalline complex forms and traps ions drastically reducing conductivity. Choosing optimal salt is also a point that must be addressed. Salt must be electrochemically stable to prevent oxidation or reduction when potential is applied. Mobility of the anions is also essential for optimization. Mobile anions can cause polarization of anions, and the resulting concentration gradient will affect conductivity. Because of that, large and immobile anions should be used, for example, ClO_4^- or PF_6^- . Using different salts in a composite can increase the conductivity of the composite. It can be explained considering a higher degree of salts dissociation and higher configurational entropy preventing crystalline complex from forming. Additionally, introducing low molecular mass molecules that help salts to dissociate can increase the concentration of the salts before the crystalline phase forms and increase ion mobility [50].

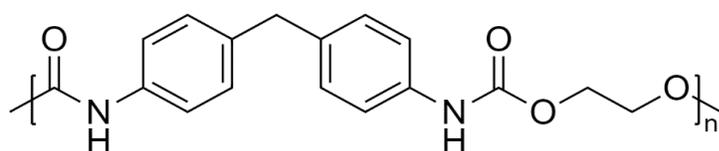
3. Experimental methods

This chapter gives a detailed overview of the materials and equipment used in this thesis. It further lays out the experimental techniques with which devices were fabricated and analyzed. All experiments were conducted at ambient conditions.

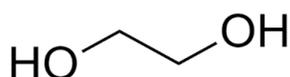
3.1. Materials

If not declared otherwise, all substances were purchased from commercial suppliers and used without further purification.

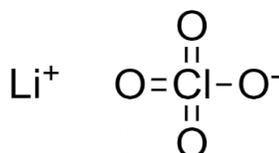
PEDOT:PSS	Clevios S V4, Germany
NaOH	Sigma Aldrich, > 98 %, Germany
Waterborne polyurethane dispersion	Alberdingk U3251, Germany
Ethylene glycol	Sigma-Aldrich > 99 %, Germany
Triton™ X-100	Sigma-Aldrich, Germany
Lithium perchlorate	Sigma-Aldrich > 99.8 %, Germany



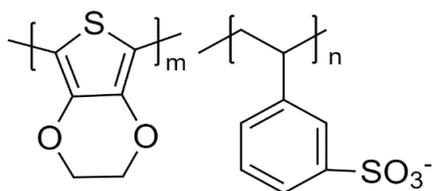
Termoplastic polyurethane



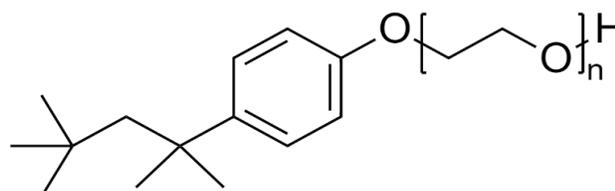
Ethane-1,2-diol / ethylene glycol



Lithium perchlorate



poly(3,4-ethylenedioxythiophene)
polystyrene sulfonate / PEDOT:PSS



2-[4-(2,4,4-trimethylpentan-2-yl)phenoxy]ethanol /
Triton X-100, where $n_{\text{average}} = 9.5$

Figure 6. The structural formula of materials and reagents used during this work.

3.2. Experimental procedures

Synthesis of PEDOT: PSS/PU composite: PEDOT:PSS was mixed using a magnetic stirrer for 15 minutes (1000 rpm) to homogenize the mixture and then left to rest for another 15 min for all air bubbles to disappear. A corresponding amount of NaOH 0.1 M solution was added to increase the pH value. After that, various PU dispersion amounts were added dropwise and mixed for another 15 minutes. The screen-printing method was used to deposit the composite mixture onto polypropylene to form a thin electrochromic composite. An aluminum frame with 77 polyethylene terephthalate threads per 1 centimeter was used to fabricate thin film dried at 100 °C for 1 hour manually and then cooled down to room temperature.

Synthesis of stretchable PU electrolyte: PU dispersion together with additives (0.1 M NaOH, Triton X-100) was added to chemical glass and mixed for 15 minutes (1000 rpm). 1 M LiClO₄ solution was added dropwise to stirred mixture. PU mixture was transferred to polypropylene mold and left to cure for 3 hours at 60 °C.

Transfer of composite onto PU substrate: Electrochromic composite was heated 20 minutes to 100 °C then PU substrate was firmly pressed onto composite and heated for another 20 minutes. PU substrate with electrochromic composite were peeled off the polypropylene mold and left to cool down at room temperature.

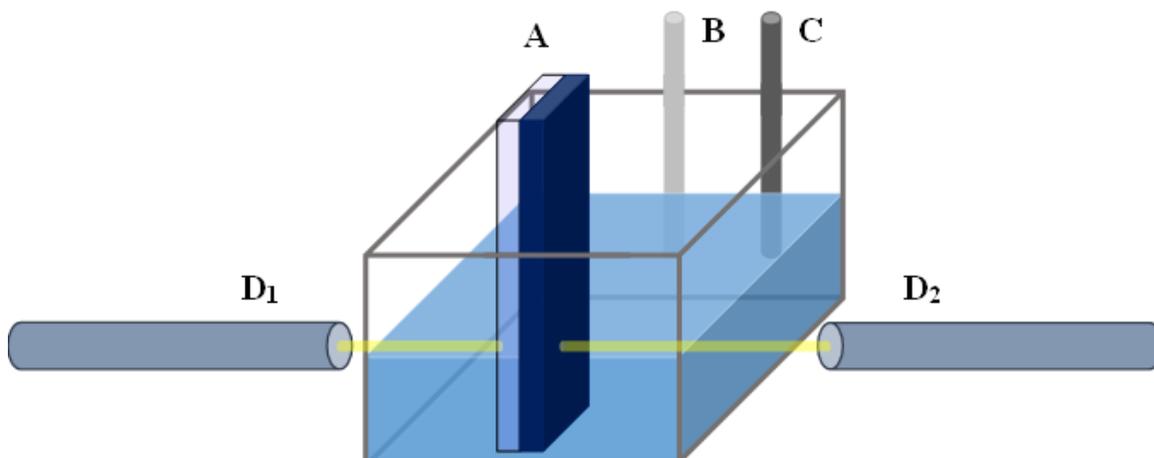


Figure 7. Representation of setup for electrochromic evaluation of PEDOT:PSS/PU composite. Custom built setup for the measurement of electrochromic properties: A – PEDOT:PSS / PU sample as working electrode; B – reference electrode; C – platinum counter electrode and D₁, D₂ – optical fibers directed from a light source through the sample to the spectrophotometer Ocean Optics USB4000.

Color change evaluation: Color change was measured using the standard three-electrode system with fiber optic cables connected to a spectrophotometer (Figure 7). The electrochromic composite was connected to the working electrode, as a reference electrode Ag/Ag⁺ in 0.5 M KCl was used, and platinum wire was the counter electrode. The redox state of the composite was altered using chrono-amperometry. A potential of +1 V was applied for 5 seconds, and

a -2 V potential for 15 seconds. Color change was characterized by measuring light transmittance at 600 nm, where the highest difference in light absorption between oxidized and reduced states was observed.

A conclusive procedure to evaluate the color difference between colored and colorless states of electrochromic composite must be used in all measurements to have comparable results. Transmittance at one specific wavelength can be used to evaluate color change. This wavelength is usually chosen where is the biggest difference in absorbance between the colored and transparent state of the material. The highest difference between the two states for PEDOT:PSS can be observed around 600 nm (Figure 8) and is calculated using this formula:

$$\Delta T = |T_{Colored} - T_{Bleached}| \quad (2)$$

The more significant ΔT value, the more visible the optical change occurs. Thus, it is necessary to maximize the ΔT value to achieve the composite with the most noticeable color change.

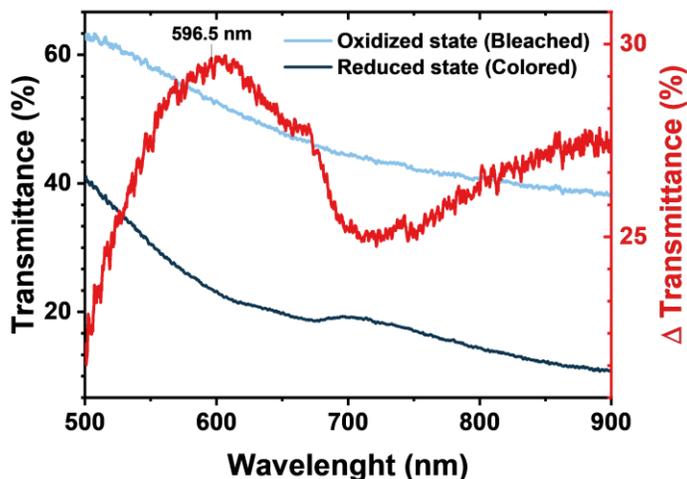


Figure 8. Transmittance spectra for electrochromic composite. Reduced and oxidized state spectra are presented in black and blue colors respectively, the differential spectrum marked with red. $\Delta T_{max} \approx 600$ nm, which was used to evaluate color difference.

Resistance measurement with different strains: Samples were placed in a custom-made isolated metal frame with a multimeter electrode attached to each side of the sample and stretched to the desired length to measure its resistance. Measured resistance was used to calculate the resistivity of the samples.

Raman spectra characterization: Raman spectra of films were acquired using Alpha 300R (WITec, Germany) Raman spectrometer equipped with 532 nm laser source and thermoelectrically cooled to -60 °C CCD camera. Laser was focused by $50\times/0.8NA$ objective lens to a spot size approximately 0.81 μm . The Raman signal was dispersed by using 600 lines/mm grating. Each sample was recorded at least three different spots on its surface with 100 min acquisition time.

Atomic force microscope characterization: Surface structure was evaluated using atomic force microscope BioscopeCatalyst (Bruker, USA). Samples were measured in air, using contact mode and silicon nitride tip with reflective gold coating (tip radius 20 nm, spring constant 0.06 N/m).

Electrochromic measurements: Ocean Optics USB4000 spectrophotometer from Ocean Optics (Largo, USA) was used for optical transmittance measurements. Electrochemical measurements were conducted with potentiostat/galvanostat Autolab PGSTAT128N from ECO-Chemie (Utrecht, The Netherlands).

4. Results and discussion

This work consists of three distinct parts:

- Development and characterization of stretchable electrochromic screen-printable composite.
- Development of solid, stretchable, and transparent electrolyte using WbPUD and lithium perchlorate.
- Combing both materials to create working prototype of stretchable electrochromic cell operating in transmittance mode.

4.1. Electrochromic and stretchable composite

Before utilizing electrochromic material, it is recommended to assess these parameters: electrochromic contrast, coloration efficiency, write-erase efficiency, switching speed, stability, cycle life, and optical memory. However, developing stretchable electrochromic material has additional challenges. Its stretchability and stability at different strains should be examined as well.

4.1.1. Electrochromic composite optimization

Several parameters need to be optimized to achieve the best color change: synthesis conditions, mixture composition, and thickness.

4.1.1.1. Synthesis conditions

Two methods for electrochromic composite fabrication were considered and assessed: screen printing and drying composite mixture in a polypropylene mold. Even though forming a thin film by evaporation of composite mixture has a lot of advantages, such as simplicity, high reproducibility, and easy thickness control, the screen-printing method was chosen to fabricate electrochromic films further in this work. Reasons behind selecting the screen-printing method are: method can be easily scaled, used commercially, it can be easily used to create easy to print arrays, and it is possible to print onto a textile or even paper. However, during this work, significant drawbacks of using screen-printing method became increasingly evident: lack of reproducibility without costly equipment and difficulty in controlling the thickness of the film.

4.1.1.2. Mixture composition and sample thickness

Samples with different PU and PEDOT:PSS ratios were fabricated using screen-printing and evaluated. Composites with 50 % to 100 % of PEDOT:PSS content by weight were fabricated, and the performance of the composite was evaluated to determine the optimal amount of PU. Thickness was controlled by screen printing several layers on top of each other and drying the composite completely between each step. The thickest sample was achieved by printing three layers on top of each other and the achieved thickness varies from 0.8 μm to 5 μm . As it will be discussed later, sodium hydroxide was added to the PEDOT to increase pH and prevent polyurethane dispersion from coagulation. To determine the best composition of the stretchable electrochromic material, two main factors were considered: color change and conductivity of the composite at different strain.

To preliminary asses optimal composition of the mixture highest possible color change was measured. The highest color change was achieved by oxidizing and reducing the sample for 30 seconds. Applying potential for 30 seconds is not optimized considering longevity of the composite, the sample might degrade, and color change will decrease faster. Maintaining this color difference is not feasible for more than ten cycles. However, it is a helpful parameter to quantify the highest possible color change.

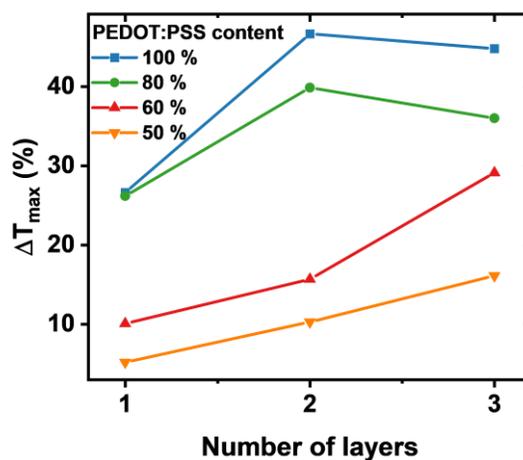


Figure 9. Calculated ΔT_{max} for composite with 50 % - 100 % PEDOT:PSS by weight with different thicknesses.

In Figure 9 the highest observed color change is presented for the samples ranging from 50 % to 100 % of PEDOT:PSS. Each composite sample with one, two, and three deposited layers were characterized. Samples with three layers and more than 80 % PEDOT:PSS seem to exhibit smaller color changes than samples with two layers. In comparison, the samples with less than 60 % PEDOT possess reverse property. If samples in their bleached state are already dark, an additional color change is less visible. Thus, ideally, composite needs to be thin enough to be almost transparent in their bleached form, while having deep blue color in reduced state. Based on this data, it was decided that samples with 50 % and 60 % of PEDOT:PSS show too small color change and thus are sub-optimal samples and will not be discussed in future of this work.

4.1.2. Stretchability characterization

Stretchability is another essential parameter to consider while determining optimal mixture composition. During the last measurement, it was determined that PEDOT:PSS content must be higher than 60 %.

It is crucial to determine at what strain samples with different amounts of PEDOT:PSS lose their conductivity and thus, cannot display visible color change. A custom-made frame was built to measure this, where samples could be secured, and their resistance measured.

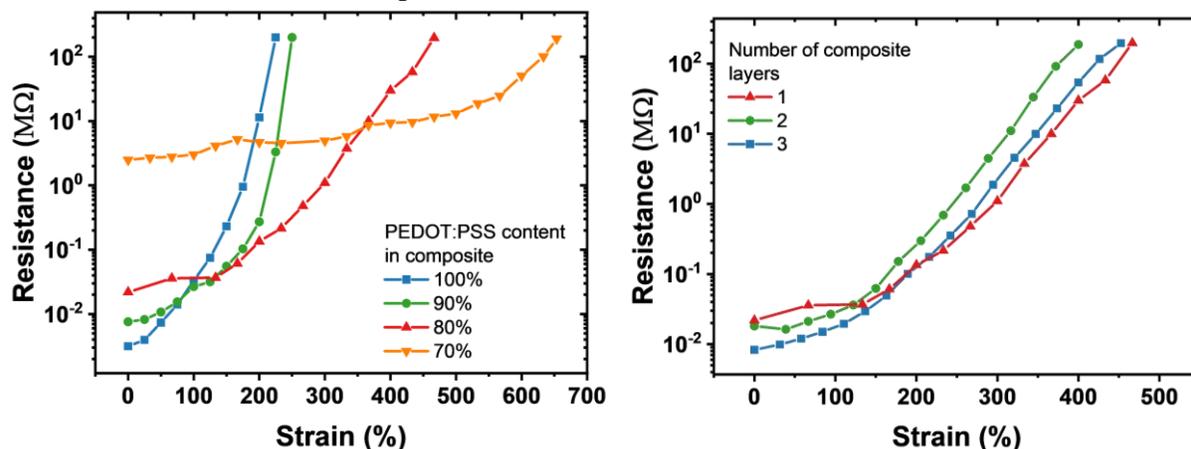


Figure 10. Resistance at different strains was measured. The dependence on PEDOT:PSS content (left) and number of layers (right) were evaluated.

Figure 10 (left) shows the resistance of the stretchable composite at different strains. As expected, a sample with no polyurethane has the lowest resistance at 0 % strain. However, its conductivity decreases rapidly during elongation, and finally, samples resistance is close to 200 MΩ at 200 % strain. Samples with 10 % and 20 % polyurethane have slightly higher resistance at 0 % strain and can be stretched out up to 225 % and 475 %, respectively. Sample with the lowest amount of PEDOT:PSS has the highest resistance at 0 % strain; however, it can be stretched out up to 650 % elongation and present similar resistance as the sample with no polyurethane at 200 %. This data shows that an 80 % PEDOT:PSS sample is optimal if a strain up to 350 % is expected; however, if a bigger strain is expected 70 % PEDOT:PSS sample should be used. Using this data, it was decided to continue characterizing 80 % sample.

Samples with the same composition and different thicknesses were characterized to determine how thickness changes the stretchability of the composite. Samples with 80 % of PEDOT:PSS and one, two, and three layers of the electrochromic composite were tested similarly.

Another way to characterize conductive material is to calculate its sheet resistance. It is commonly used to characterize semiconducting materials, thin film metal, and glass coating. This is extremely valuable parameter characterizing thin film samples, because it is not dependent on size of the sample, thus, can be used to compare materials with different geometry.

Resistance of the thin film was measured, and sheet resistance was calculated using following formula:

$$R = \frac{\rho L}{t W} \rightarrow \frac{R W}{L} = \frac{\rho}{t} = R_{sheet} \quad (3)$$

R – Resistance (Ω)

ρ – Resistivity (Ωm)

L – Length (m), current flows parallel to the length of material

W – Width (m)

T – Thickness (m)

R_{sheet} – Sheet resistance (Ω / \square , ohm per square)

It can be seen that sheet resistance (Figure 11) is a bit higher than reported in the literature [51,52]. Sheet resistance registered in this work is around $10^3 \Omega / \square$, while in different research it ranges from 50 to 202 Ω / \square . Also, the sheet resistance differs if different ratio of PEDOT:PSS and PU is used. The higher the amount of PEDOT:PSS the lower the resistance is obtained. This principle is the same independently on the number of layers.

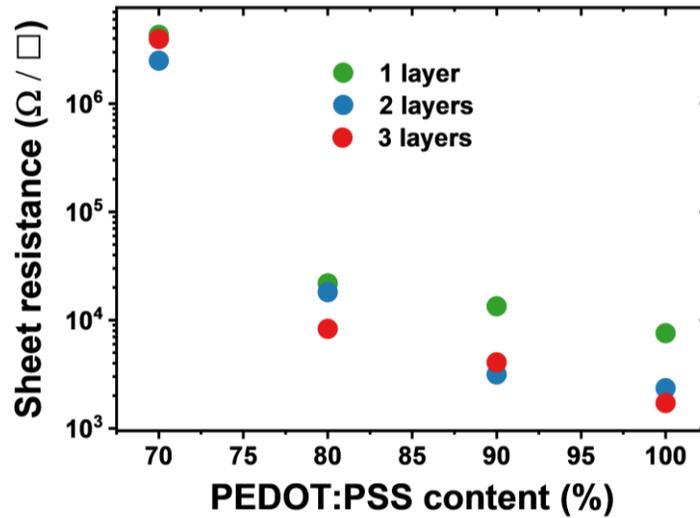


Figure 11. The measured sheet resistance of stretchable electrochromic composite with various PEDOT:PSS content and 1-3 screen printed layers.

Difference in sheet resistance between 70 % and pure PEDOT:PSS is around 3 orders of magnitude. A vital issue to address is that even though the resistance of the composite was measured, there were two components to it: resistance of the sample and contact resistance, which is possible to disregard only if a 4-probe station to measure resistance is used. This resistance was measured using a multimeter; thus, it must be addressed.

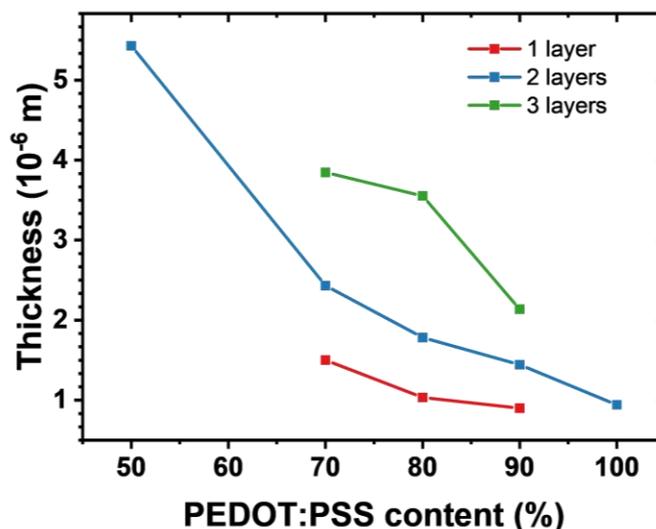


Figure 12. The measured thickness of the screen-printed electrochromic composite with various PEDOT:PSS content and number of layers.

Sample thickness was measured using a profilometer (Figure 12). Best color change with significant stretchability possesses a sample with 80 % PEDOT:PSS. The thickness of that sample is equal to around one micron. And with each additional layer thickness of the film increases. Additionally, samples with higher PU content have higher thickness. This is due to the density difference between PEDOT:PSS and PU. Solid PEDOT:PSS is much denser than used polyurethane. Used polyurethane dispersion density is equal to 1.08 g/cm³ while PEDOT:PSS is 1.45 g/cm³ [53,54]. This increases thickness when PU content (%) increases.

4.1.3. Color change evaluation

Figure 13 (left) shows how the transmittance at 600 nm changes when positive and negative potential is applied. Applying positive potential (+1 V) oxidizes sample and it becomes almost transparent which results in increased transmittance. If negative voltage is applied (-2 V), sample is reduced, transmittance drops, and sample becomes deep blue color. Oxidizing and reducing the sample once is considered one cycle. Custom C program was written to find peaks and calculate ΔT , necessary to quickly analyze large amounts of data generated by this characterization. In some cases, (Figure 13(right)), a rapid decrease of change in transmittance can be observed in the beginning of the test. It can be explained by loose chains of polymer being washed away by the solution. After initial drop ends, in around the 10th cycle, ΔT stabilizes and there is no significant drop at least until 50th cycle.

In all future electrochromic measurements this type of analysis will be conducted to evaluate color change of the material.

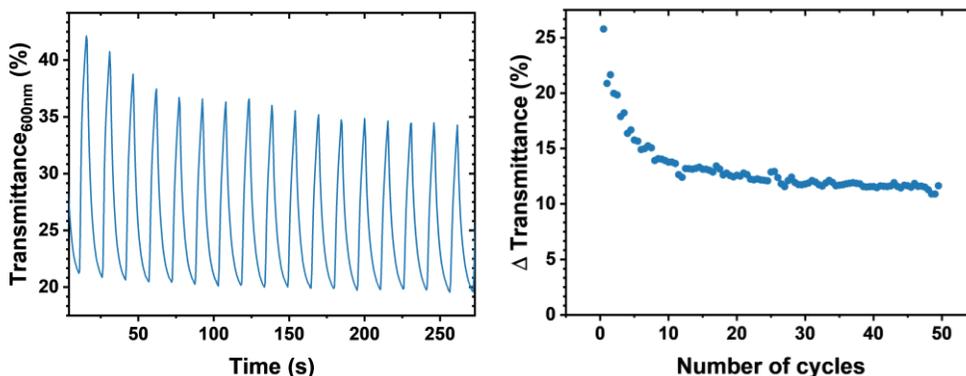


Figure 13. Transmittance changes when the different potential is applied (left). The sample was oxidized using +1V for 5 s and reduced to its colored state by applying -2 V potential for 10 s. After obtaining peak values, ΔT was calculated (right).

4.1.4. Electrochromic contrast of PEDOT:PSS composite

Electrochromic contrast was measured and calculated for samples ranging from 70 % PEDOT:PSS to 100 % PEDOT:PSS (Figure 14). Oxidation and reduction potential was +1 V and -2 V, while duration was 5 and 12 s, respectively. These potential and duration times were chosen according to literature [16]. As it can be expected sample with highest amount of PEDOT:PSS (100 %) has highest ΔT , while sample with least PEDOT:PSS (70 %) has lowest ΔT . Samples with 100 % and 90 % PEDOT:PSS have a slight decrease in ΔT , while samples with 80 % and 70 % do not. This can be explained by higher amount of polyurethane that creates matrix and surrounds PEDOT thus it is less likely to be washed away by solution.

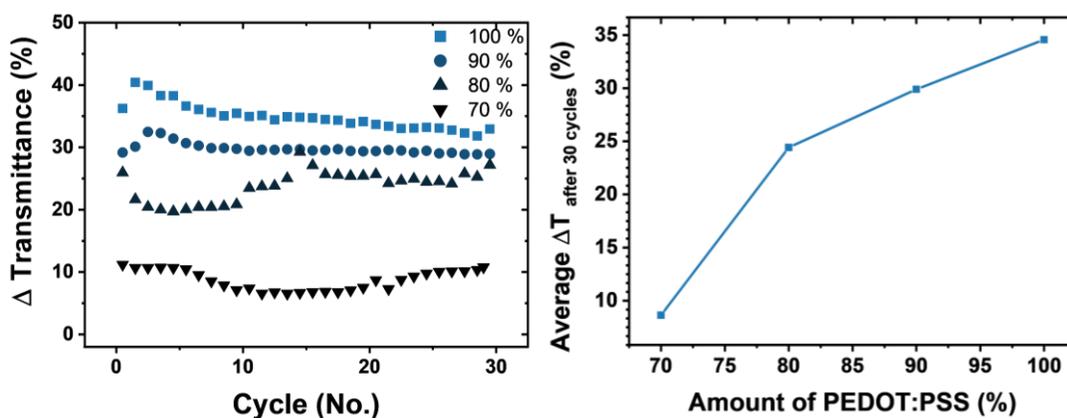


Figure 14. ΔT dependance on the number of cycles applied to the samples with different PEDOT:PSS and PU ratio was measured. For 100 % and 90 % sample ΔT decreased by few percent, while samples with 80 % and 70 % PEDOT:PSS no significant decrease in ΔT was observed (left). Representation of electrochromic contrast change with different amounts of PEDOT:PSS 70 % - 100 % (right)

Sample with 70 % PEDOT:PSS demonstrates ΔT equal to 8.6 %, samples with 80 % and 90 % of PEDOT:PSS show 24.4 % and 29.9 % ΔT respectively and a 100 % sample displays a 34.7 % color change (Figure 14). These values are comparable with other work [55].

4.1.5. Coloration efficiency

Coloration efficiency is one of the necessary parameters to consider before electrochromic material can be used practically. This value quantitatively describes how the color of the material changes per intercalated or extracted charge. This value is calculated using a change in optical density at a particular wavelength, and an electric charge is used to apply that change. It can be described using this formula:

$$CE(\lambda) = \frac{\Delta OD(\lambda)}{Q} = \frac{\lg \frac{T_b}{T_c}}{Q} \quad (4)$$

CE – coloration efficiency

T_b and T_c – transmittance in bleached and colored state

λ – wavelength at which CE is measured

$\Delta OD(\lambda)$ – change in optical density at wavelength λ

Q – charge used for the color change, integration of the current versus the coloration time

Calculated coloration efficiency (Figure 15) is comparable with other research, which shows that application for this electrochromic composite could be possible considering color change and energy efficiency. In this work highest achieved coloration efficiency in the composite is 220 cm^2/C while in other research it ranges from 80 cm^2/C to 440 cm^2/C [7,8,24,56].

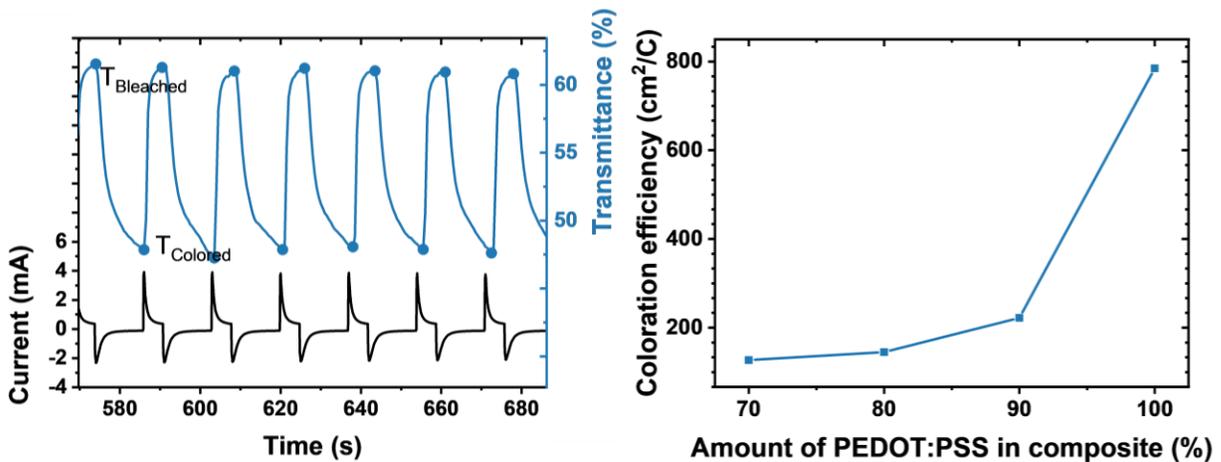


Figure 15. Using the transmittance at 600 nm and current (left) to oxidize and reduce the sample coloration efficiency was calculated (right).

Coloration efficiency significantly decreases when a minimal amount of polyurethane is added. However, with each further addition, it diminishes less. It can suggest that lower content of PEDOT:PSS makes electrochromic material less efficient, because color change is less apparent.

4.1.6. Ethylene glycol as an additive to the electrochromic composite and its influence on surface of the film

A plasticizer can be added to a polymer mixture to increase flexibility, plasticity and to decrease viscosity and friction during manufacturing step. Adding plasticizer helps screen printing process and regulates viscosity of the mixture as well as lowers surface tension of the mixture, and it was necessary to screen print composite successfully. For this purpose, ethylene glycol was chosen. Additionally it is reported that adding ethylene glycol can increase conductivity of PEDOT:PSS and improve long term stability [28,29].

To investigate influence of ethylene glycol on PEDOT:PSS/PU composite samples were analyzed using AFM. The morphology of PEDOT:PSS/PU composite with and without added ethylene glycol was analyzed using contact mode in air. Thin films were obtained using the screen-printing method, as described before. Two samples were investigated: with and without added ethylene glycol. Surface structure of polymers can be seen in Figure 16.

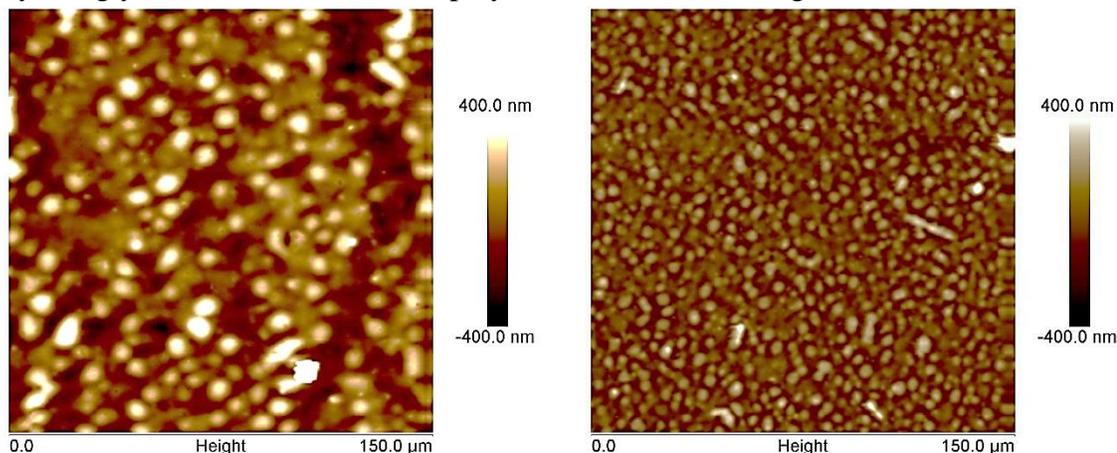


Figure 16. The morphology comparison of composite without (left) and with (right) EG.

The PEDOT:PSS film without added ethylene glycol consists of aggregates with a diameter of around eight microns. The PEDOT:PSS and PU agglomerates are dispersed evenly in the film. With the addition of EG, the morphologies of PEDOT:PSS films change obviously, and the size of the grains decreases to 3.5 μm . This can be explained by lowered surface tension where ethylene glycol works as a surfactant. Composite with added ethylene glycol has lower surface tension, resulting in better blending between two polymers and smaller aggregates. This concludes that adding ethylene glycol to the composite mixture not only lowers surface tension, improving screen printing process, but can improve long term PEDOT:PSS stability as well.

4.1.7. Raman analysis

Raman analysis (Figure 17) was conducted to further characterize composite. For pristine PEDOT:PSS, primary peaks at 1257, 1422, and 1533 cm^{-1} are attributed to $\text{C}_a\text{--C}_{a0}$ inter-ring stretching vibration, $\text{C}_a\text{=C}_b$ symmetric stretching vibration on the PEDOT chain, and $\text{C}_a\text{=C}_b$ asymmetrical stretching vibration, respectively [29,57]. The primary peak shifts from 1422 cm^{-1} to 1408 cm^{-1} could be registered then PEDOT:PSS and a mix of PEDOT:PSS and PU is compared. The blue shift indicates that a composite PEDOT:PSS is more reduced than pristine PEDOT:PSS. This can be explained by considering added sodium hydroxide to balance the pH of the composite. This corresponds with the observed redshift when HNO_3 or HClO_4 is added [26,29,31,52].

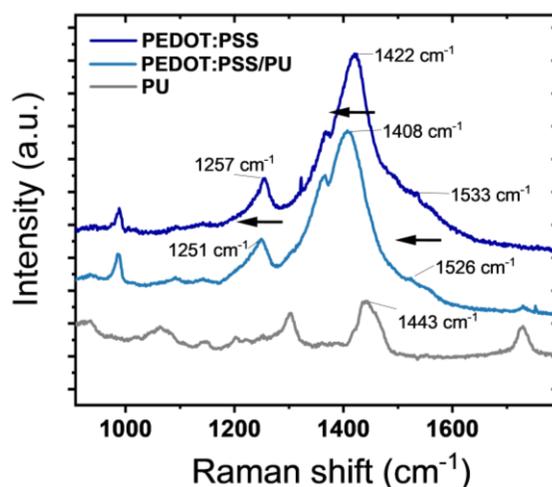


Figure 17. Raman spectra for pristine PEDOT:PSS, 80 % PEDOT:PSS composite and pristine PU is presented. Three peaks presented here have slight shift to the left compared to pristine PEDOT:PSS.

4.2. Solid, stretchable, and transparent electrolyte development

To create an electrolyte that satisfies all the requirements, two things must be considered: stretchable base and charge carrier. Inorganic materials are highly brittle; thus, almost impossible to make stretchable electrolytes. Elastomers are simple and straightforward materials that can be used as a stretchable base for the electrolyte. Polymer-based electrolytes are easily processable using solution casting, thus being a great material for large-scale manufacturing processes. Additionally, if wearable electronics is considered as an application for the stretchable electrolyte, the polymer must be biocompatible and nontoxic. Crucially, it must be transparent. Considering

that stretchable electrochromic composite is based on polyurethane, this polymer is a feasible candidate for creating solid, stretchable, and transparent electrolytes. Then, phase separation between the electrolyte and electrochromic material would be minimal.

Choosing proper electric charge conductors has much more variables. Electric charge carrier needs to have as low resistance as possible to make devices more efficient. It should not absorb radiation in the visible light spectrum to ensure clear visibility of the color change in the electrochromic device. However, the minimal coloration of the electrolyte would be acceptable if it would compensate for the quick switching time of the device. Phase separation should be avoided by ensuring that the charge carrier is compatible with the polymer matrix. Biocompatibility and price should be considered if the electrolyte is created with real-life applications.

Metal nanoparticles are fascinating materials with a lot of exciting applications. For example, gold nanoparticles are thoroughly researched, and there are numerous fabrication methods with accurate size control. Unfortunately, nanoparticles are cytotoxic and absorb radiation in the visible light region. This would heavily limit the concentration of nanoparticles and conductivity as well [58–60]. Carbon nanotubes and conductive polymers, such as polyaniline or poly-pyrrole, could not be considered due to their intense color and thus making it impossible to make transparent electrolytes [61]. Ionic liquid could be used as a transparent alternative; however, phase separation possibility and price would be factors that would significantly limit its use [62,63].

A great alternative to previously mentioned materials is lithium salts. Lithium salts are widely used in making a lithium-ion battery. Salts with lithium cations are used due to the size of the ion, resulting in higher charge mobility and a higher charge to the mass ratio, which makes batteries recharge faster and with a higher specific energy. Various anions are used to make electrolytes for research purposes and commercial applications: ClO_4^- , $(\text{BF}_4)^-$, $(\text{PF}_6)^-$. These anions combine excellent ionic conductivity and electrochemical stability. During this research, lithium perchlorate was used for the reasons of cost and convenience. Lithium perchlorate is readily available and is not absorbing radiation in the visible light spectrum.

4.2.1. Polyurethane-based solid stretchable electrolyte.

Often to create soft electronics silicon rubber is used, as they have great environmental stability and low toxicity. However main issue is that these types of materials, for example polydimethylsiloxane, is highly hydrophobic, thus it is extremely difficult to combine it with water processable material such as PEDOT:PSS. Another requirement for polymer matrix is that it must be compatible with electrochromic composite and adhere completely without any phase separation. The easiest way to achieve that is to use same polymer as in stretchable electrochrome: polyurethane. This polymer is known for being stretchable, transparent, and biocompatible for potential bio-application, can be created as waterborne dispersion, which allows to manufacture it without need of organic solvents. Because of the reasons mentioned above it was

decided to investigate and create solid, transparent, and stretchable electrolyte using water borne polyurethane.

4.2.2. Waterborne polyurethane dispersion stability

During this research, one of the significant issues was the stability of waterborne PU dispersion (WbPUD). This dispersion is essential to this work because it was chosen to consider biocompatibility and the materials' environmental impact. Used PEDOT:PSS products were water-based (PH1000) or water-soluble (Clevios S V4). This was the driving force to use waterborne polyurethane, and other methods of polyurethane synthesis were not feasible. There were no other viable alternatives to waterborne polyurethane dispersion. Used dispersion was commercially available industrial adhesive and sealants used for automotive adhesives and lamination applications with low stability to outside conditions, such as pH and ionic strength of the media.

However mixing WbPUD with PEDOT:PSS and lithium perchlorate solution resulted in coagulation of the polyurethane. It was believed that the reason behind coagulation was a rapid mixture of two substances, and PEDOT:PSS or lithium perchlorate solution was slowly added dropwise to WbPUD. Cooling of components and heating them before fabricating the mixture was also tried. However, these methods did not improve the stability of WbPUD. Similar to other PEDOT:PSS sources, such as PH1000 or HTL Solar, Clevios S V4 is highly acidic with pH being around 2. Simply mixing PEDOT:PSS with WbPUD results in quick coagulation of polyurethane, resulting in a nonuniform mixture unusable for screen printing.

Table 1. Different composition of a mixture trying to stabilize WbPUD with LiClO₄ solution with time before coagulation occurred.

No.	V _{WbPUD} , ml	V _{Triton-X 100} , ml	V _{NaOH(0.1 M)} ml	V _{LiClO₄(1 M)} , ml	Time before coagulation, min
1	1	-	-	0.5	0.5
2		-	0.1	0.5	1
3		-	0.2	0.5	1
4		0.01	-	1.5	30
5		0.05	-	1.5	45
6		0.1	-	1.5	45
7		0.05	0.1	0.7	stable
8		0.05	0.1	1.3	stable
9		0.05	0.1	1.5	stable
10		0.05	0.1	1.7	10

Two different ways to prevent coagulation were used for PEDOT:PSS to achieve successful fabrication: adjusting the pH of the PEDOT:PSS by adding 0.1 M NaOH solution and adding surfactant (Triton-X 100) to WbPUD before mixing it with PEDOT:PSS. Addition of Triton-X 100 had no desired effect. Adding small (0.16 ml for 1 ml of WbPUD) amount of 0.1 M NaOH solution to increase pH solved the issue. Thus, it is believed that pH was the main factor that prevented successful mixing of two polymers.

A similar issue arose when WbPUD was mixed with lithium perchlorate solution. Stabilization WbPUD with LiClO_4 was a slightly more challenging. After few preliminary tests it occurred that mixing order did not have any influence on coagulation of the PUD. Different test runs were conducted to determine highest amount of LiClO_4 to ensure highest conductivity of the electrolyte (Table 1). Even though LiClO_4 is neither acidic nor basic salt it was tried to stabilize it with NaOH solution using stabilization of PEDOT:PSS/PU mixture as an example. Slight effect was noticed, however not significant enough. Addition of Triton-X 100 stabilized the mixture slightly more. Combining these two approaches resulted in a mixture that was stable at least 24 hours with 1.5 ml LiClO_4 1 M solution added to 1 ml of WbPUD. Reason behind this coagulation in a media with a neutral pH can be explained by high ionic strength. This process is similar to “salting-out” of proteins used in biotechnology [64]. Adding Triton-X 100 stabilized dispersion and made polyurethane softer, however, made electrolyte hygroscopic (discussed in 4.2.4. chapter).

It must be addressed that the pH of the PEDOT:PSS source was already optimized in the product to ensure the best shelf life, stability, and conductivity. Changing the pH of the media can lower the conductivity of PEDOT:PSS. However, it was a necessary adjustment to keep using WbPUD, which had no feasible alternatives. Even with these improvements, WbPUD was not stable if a 1.0 M solution of lithium perchlorate or higher was added.

4.2.3. Lithium perchlorate dissolving in PU matrix and phase separation of the salt

Even though Triton-X 100 was mainly used to prevent polyurethane dispersion from coagulation, it performs one additional role. Lithium ions and lithium salts are extensively used researching solid polymer electrolytes used in lithium-ion batteries. It is stated [65] that polar groups in a polymer matrix, such as —O— , —NH— , and —S— , help the cation and anion of the lithium salt to dissociate. Those groups are present in polyurethane and help to dissolve lithium salt. However, Triton-X 100 structure contains a lot of —O— groups, where lone pair of oxygens on the poly(ethylene glycol)segment is coordinated to the lithium-ion by Coulombic interaction. Polyethylene glycol was also considered an additive to increase the solvation of the salt; however additional Triton-X 100 would be necessary to stabilize the polyurethane dispersion.

4.2.4. Hygroscopicity of PU-based stretchable transparent electrolyte

During EIS measurement of PU-based stretchable transparent electrolyte, it was noticed that impedance diagrams varied a lot between the measurement even if no changes were made to the material or measurement conditions. Diagrams shifted consistently with each measurement. It suggested that something was changing with passing time. It was also noted that the composite became soft and gel-like after the electrolyte was in ambient conditions for an extended time (1 hour or more).

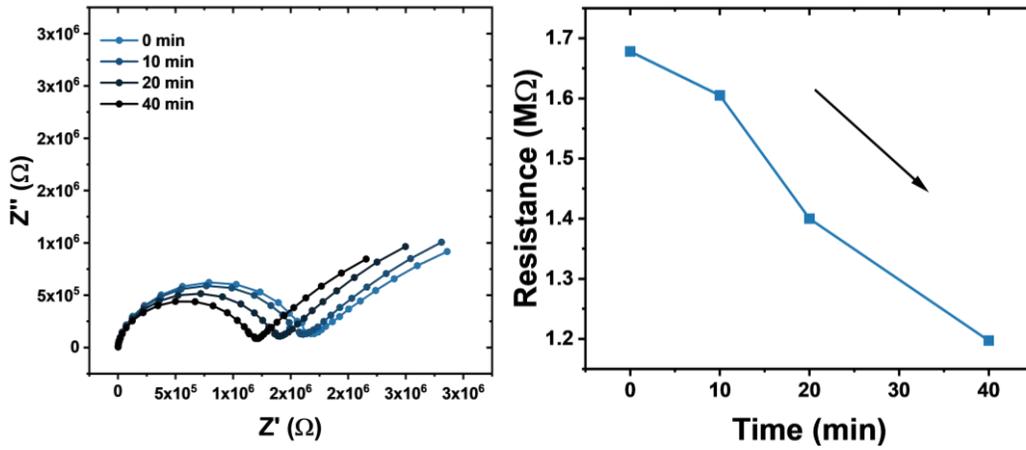


Figure 18. Change in impedance spectra measured after keeping sample in air at different period of time(left). Change of resistance that was calculated from EIS spectra after drying stretchable electrolyte. (right)

Analyzing EIS spectra was noted that spectra shifted consistently during the regular time intervals. It was pointed out that resistance decreased with time (Figure 18). The only possible explanation was that the charge mobility increased while the electrolyte was in an ambient atmosphere. Part of the spectra was fitted with the circle to calculate the change in resistance of the material. Increased conductivity can be explained considering following formula:

$$\sigma = \frac{q_i^2 c_i}{k_B T} D_i \quad (5)$$

σ – ionic conductivity (S/cm)

q_i – charge of solute (C)

c_i – concentration of species i (mol/cm³)

k_B – Boltzmann constant (1.38054×10^{-23} J/K)

T – temperature (K)

D_i – diffusivity of solute i (cm²/s)

Two main forces can drive lithium ions to relocate: externally applied potential or concentration gradient [48]. Ion mobility relates to how easy can ions move if external electrical field is applied, while diffusivity shows how ions move under the influence of concentration gradient. Even though diffusivity and ion mobility are treated as two distinct phenomena, it can be shown that they are the same physical entity [48]. This shows that relation discussed before still holds. As other parameters could not change (charge of solute, concentration of ions, temperature) the only way for the conductivity to increase is increased ion diffusivity – thus ion mobility.

This change can be explained by addressing the hygroscopic properties of added Triton-X 100. It means that surfactant draws moisture from air making stretchable electrolytes more conducting and gel-like after prolonged exposure to ambient conditions. This naturally is a problem because the electrolyte is not stable in the room atmosphere. This is hugely challenging; it means that the results of electrolyte characterization might be distorted. To prevent this, the stretchable electrolyte was dried at 100 °C for 1 hour before every measurement. In the future, this problem can be solved by adjusting the amount of Triton-X 100 used, considering the hygroscopic properties of Triton-X 100.

4.3. Electrochromic stretchable device

As a proof of concept, an electrochromic device based on developed electrochromic material and stretchable electrolyte was fabricated and tested. A fabricated electrochromic device operates on the transmittance mode where the ion storage layer is the same as the electrochromic layer. This results in the symmetric device, where if a positive voltage is applied, one part of the device becomes deep blue, and if a negative voltage is applied, another part becomes deep blue (Figure 19).

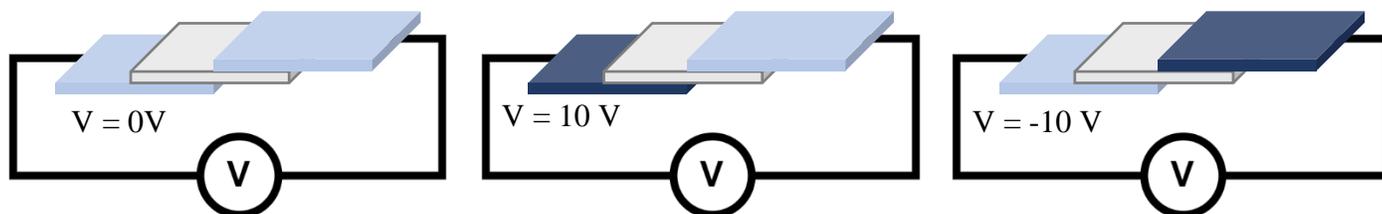


Figure 19. Working scheme of the constructed electrochromic stretchable device with different potentials applied.

The constructed device was connected to DC regulated power supply, and the lowest potential was applied sufficient to induce a color change. The color change was registered using a digital camera and analyzed using ImageJ software based on methods described in a paper [16]. The calculated mean grey value represents a color change in the device (Figure 20).

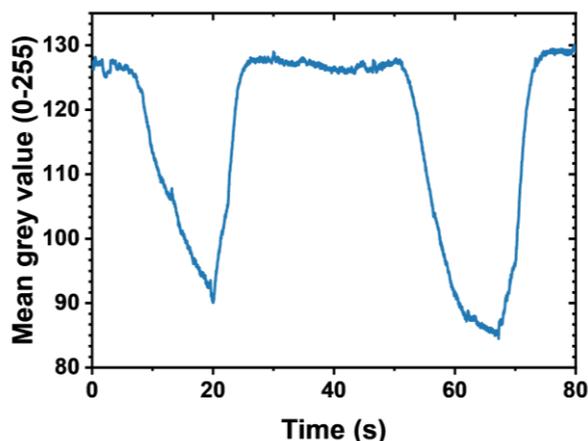


Figure 20. Color change of the stretchable electrochromic device when + 10 V potential is applied. Mean grey value was generated from the stack of photos generated by ImageJ software.

The constructed device (Figure 21) switches on and off slower than the electrochromic composite measured in the KCl solution. This is due to the lower ion mobility in the polyurethane-based electrolyte.

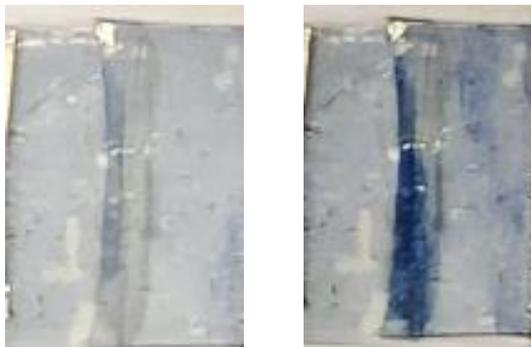


Figure 21. Photo of developed electrochromic device in colorless state (left) and colored state (right).

The primitive design of the electrochromic stretchable device results in a slow response time, uneven color change, and requires a high potential to induce a color change. However, it is already proven that the performance of the stretchable electrochromic material is comparable with other works. The performance of the electrochromic device can be improved by making the electrochromic device smaller, developing new material for the ion storage layer of the device, and optimizing the thickness of the stretchable electrolyte. It is an engineering challenge to optimize the device and improve its performance.

5. Conclusions

- After investigating stretchable and electrochromic PEDOT:PSS/PU composite it was determined that highest electrochromic contrast is achieved with high PEDOT:PSS content ($\geq 90\%$), however in that case sample irreversibly deteriorates after strain of 200%. Sample with 80% PEDOT:PSS can withstand strain up to 350%, while sample with 70% PEDOT:PSS can be stretched out 6 times of its original size with no significant increase in resistance.
- Solid, stretchable, and transparent polymer-based electrolyte was created mixing polyurethane dispersion with lithium perchlorate. Amount of lithium perchlorate added to the dispersion is limited by the stability of dispersions stability, that can be further enhanced by adding surfactants. Added amount and properties of surfactant should be considered because of possible hygroscopicity of the electrolyte. Highest conductivity was achieved with 1.5 mmol of lithium perchlorate for 1 ml of WbPUD added, when mixture was additionally stabilized using TRITON-100 X.
- A working prototype of the stretchable, printable electrochromic device using PEDOT:PSS as the electrochromic material was successfully developed and tested to show successful color change. Developed PEDOT:PSS/PU composite and solid electrolyte are suitable for development of electrochromic cell, which operates on transmittance mode.

Achievements

Conferences:

- Development Of Elastic PEDOT:PSS-Based Electrochromic Composites for Stretchable Electronics Applications (poster presentation) **Juzef Kucinski**, *Mindaugas Gicevicius, Lina Mikoliunaite. Open Readings, Vilnius, Lithuania, 2021.*
- Development of PEDOT:PSS-based Screen-Printing Inks for Stretchable Electrochromic Thin Films (poster presentation). **Juzef Kucinski**, *Mindaugas Gicevicius, Lina Mikoliunaite. Advanced Materials and Technologies, Palanga, Lithuania, 2021.*
- Tampraus Elektrochrominio Kompozito Sintezė Ir Savybių Optimizavimas (oral presentation). **Juzef Kucinski**, *Lina Mikoliunaite. LMT studentų konferencija, Vilnius, Lithuania, 2021*
- Statistical Analysis of Organic Electrochemical Transistors with Photopatternable Solid Electrolyte (oral presentation). **Juzef Kučinski**, *Hsin Tseng, Lina Mikoliūnaitė, Karl Leo, Hans Kleemann. Open Readings, Vilnius, Lithuania, 2022.*

Projects:

- Project „Tamprių elektrochrominių kompozitų sintezė bei optinių savybių optimizavimas“, 2020 11 01 – 2021 04 30, No. 09.3.3-LMT-K-712-22-0289.
- Project „Tampraus bei optiškai skaidraus elastomero pagrindo elektrolito sukūrimas ir sudėties optimizavimas“, 2021 07 05 – 2021 08 31, No. 09.3.3-LMT-K-712-24-0191.

Internships:

- Internship in Technical University of Dresden, Germany as a part of the Erasmus+ program. Internship topic: „Statistical analysis of organic electrochemical transistors with solid photo-patternable electrolyte” (2021 09 01– 2022 02 02).

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SANTRAUKA

VILNIAUS UNIVERSITETAS CHEMIJOS IR GEOMOKSLŲ FAKULTETAS

JUZEF KUČINSKI

Tamprus elektrochrominio prietaiso kūrimas naudojant šilkografiniu metodu spausdintą PEDOT:PSS bei tamprų elektrolitą

Organinė elektronika yra alternatyva įprastiems silicio ir pereinamųjų metalo elektronikos gaminiams dėl mažesnių gamybos kaštų, ekologiškumo ir tamprumo. Poli(3,4-etileno dioksitiofeno) polistireno sulfonatas (PEDOT:PSS) yra dažnai naudojamas kuriant organinę elektroniką. PEDOT:PSS gali būti randamas organiniuose elektrocheminiuose tranzistoriuose, skaidriuose elektrodoose, jutikliuose bei elektrochrominėse celėse. Elektrochromizmas yra reiškinys, kai medžiagos spalva pasikeičia dėl elektronų perdavimo veikiant elektrocheminiam potencialui. Dėl nebrangių medžiagų, energijos vartojimo efektyvumo ir paprastų gamybos procesų elektrochrominiai pikseliai gali būti alternatyva įprastiems LED pikseliams. Polimerinės elektrochrominės medžiagos naudojamos kuriant tamprią elektroniką naudojant šilkografinį spausdinimą dėl daug didesnio elastingumo ir minkštumo lyginant su įprastomis neorganinėmis medžiagomis. Šilkografijos technologija leidžia ekonomiškai ir paprastai sukurti plonas plėveles pakankamai didele raiška, išlaikant greito prototipų kūrimo proceso galimybes. Elektrochrominiai įrenginiai yra pigesnė, energiją taupanti alternatyva įvairiems vaizdinimo prietaisams, tačiau iš anksto turi būti sukurtas tamprus polimero pagrindu pagamintas elektrochrominis prietaisas, kurį vėliau būtų galima panaudoti konstruojant tamprų ekraną.

Šio darbo tikslas yra sukurti veikiantį tamprios elektchrominės celės prototipą. Šiam tikslui pasiekti darbo metu buvo sukurtas PEDOT:PSS ir elastomero kompozitas. Be to, naudojant elastomero vandens dispersiją ir ličio perchloratą, buvo sukurtas kietas, skaidrus, tamprus elektrolitas. Buvo aptartas dispersijos stabilumas ir pateikti keli jo gerinimo būdai, įskaitant pH reguliavimą ir papildomą stabilizavimą naudojant paviršiaus aktyvias medžiagas. Šilkografijos technologija buvo pasirinkta sukurtam PEDOT:PSS ir poliuretano kompozitui nusodinti ir panaudoti kuriant veikiantį elektrochrominio prietaiso prototipą.

SUMMARY

VILNIUS UNIVERSITY
FACULTY OF CHEMISTRY AND GEOSCIENCES

JUZEF KUCINSKI

Development of Screen Printed, PEDOT:PSS Based, Stretchable Electrochromic Device with Solid-State Electrolyte

Organic electronics is an alternative for conventional silicon and metal-based electronics, due to its lower manufacturing costs, eco-friendliness, and stretchability. Poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT:PSS) is often used in development of organic electronics. It is used in organic electrochemical transistors, transparent electrodes, sensors, and others. Electrochromism is a material phenomenon when it undergoes a color change due to electron transfer upon applied electrochemical potential. Electrochromic pixels can be a low-cost alternative for conventional displays due to inexpensive materials, energy efficiency, and facile fabrication processes. In contrast to their inorganic counterparts, polymeric electrochromic materials have much lower elastic moduli and, therefore, could be used for the development of stretchable electronics using scalable fabrication techniques, such as screen printing or roll-to-roll printing. Screen printing technology allows to create thin films cost-effectively and simply at a sufficiently high spatial resolution while retaining the capability of the rapid prototyping process. Electrochromic devices can be cheaper, energy-efficient alternatives to various screen-like devices. However, a stretchable polymer-based electrochromic device must be created beforehand to create a stretchable screen-like device.

The aim of this work is to develop working prototype of stretchable electrochromic device. To do so, stretchable PEDOT:PSS electrochromic composite was created. Additionally, solid, transparent, stretchable, and polymer-based electrolyte was produced using elastomer water dispersion and lithium perchlorate. Stability of the dispersion was discussed and several methods to improve it were presented including pH adjustment and additional stabilization using surfactants. Screen printing technology was used to deposit created PEDOT:PSS and polyurethane composite and use it to develop working prototype of electrochromic cell.