Large-Area Electrochromic Devices on Flexible Polymer Substrates with High Optical Contrast and Enhanced Cycling Stability

Sven Macher, Marco Schott,* Martin Dontigny, Abdelbast Guerfi, Karim Zaghib, Uwe Posset, and Peer Löbmann

Large-area electrochromic devices (ECDs) based on a cathodically-coloring, side chain-modified poly(3,4-ethylene dioxythiophene) (PEDOT) derivative and anodically-coloring Prussian blue (PB) are assembled by a customized sheet-to-sheet (S2S) lamination process. The ECDs with two complementary switching “half-cells”, based on flexible PET-ITO substrates, offer enhanced optical properties in terms of visible light transmission change (4–53%), contrast ratio (CR = 93.4) and color neutrality (L* = 77.9, a* = −5.9, b* = −0.6) in the bleached state. The cycling stability is monitored for up to 10 000 switching cycles (97% charge retention). The reported optical, electrochemical, and in operando (in situ) spectroelectrochemical data are obtained from small laboratory-scale ECDs (active area: 5 × 5 cm²). These results, the homogeneity of the large-area devices and the scalability of the S2S lamination process are confirmed by measurements on the large ECDs with an active area of 45 × 65 cm². This large-area electrochromic film technology with high optical contrast and enhanced cycling stability offers an excellent perspective for further development and scale-up towards pilot production and the commercialization of flexible ECDs upon their unique materials and processing characteristics.

1. Introduction

Electrochromic devices (ECDs) change their optical properties upon an externally applied voltage or current and are used for actively controlling the light and solar transmission of windows and glazing.[1–5] In state-of-the-art electrochromic (EC) windows, for architectural purposes, tungsten oxide (WO₃) and nickel oxide (NiO) are most commonly used as EC materials, enabling a highly stable and well established dimmable window technology for energy efficiency.[4,5] However, extended response time, the employment of high-energy consuming sputter processes in production, and low coloration efficiency narrow down the benefit of EC technology in application fields that go beyond the construction sector, for example, for automotive, aeronautic or ophthalmic use. Moreover, the potential for cost reduction, that is, a major obstacle for a wider utilization of EC technology, is limited.[4,5]

With respect to the continuous high-throughput roll-to-roll (R2R) production of EC films on flexible substrates, conjugated electrochromic polymers (ECPs), such as poly(3,4-ethylene dioxythiophene) (PEDOT) and its derivatives, are interesting and promising materials.[6–9] ECPs further feature a wide range of vivid colors, high optical contrast, and coloration efficiencies as well as short response times in the range of seconds and light transmission changes over 60%. A general drawback of most ECPs is the lack of a fully colorless bleached state, which is the result of an extended tailoring of the polaronic and bipolaronic absorption bands into the visible region of the electromagnetic spectrum. The residual coloration is perceived as a light blue hue in the case of non-modified PEDOT. It only becomes acceptable in the case of very thin films, which result in insufficient darkening of the colored state.[7] In this context, chemically modified PEDOT derivatives have been developed to address specific optical and process requirements.[6,7,10,11] For example in PEDOT-EthC₆ (poly(3,4-(1-(6-hexenyloxy)methyl)ethylene dioxythiophene), see Figure S1, Supporting Information, a terminal double bond in the lateral side-chain results in a higher optical contrast and color neutrality in the bleached state in comparison to non-modified PEDOT or other conjugated ECPs.[7]

PEDOT and its derivatives may be combined in an ECD with a second electrochromic or ion-storage layer as counter electrode. When the redox states of the two materials add up suitably, ECDs based on complementary switching electrodes (“half-cells”) with intense color and high transmission change can be obtained.[12–14] The above-mentioned ECPs (PEDOT or PEDOT-EthC₆) likewise

© 2020 The Authors. Advanced Materials Technologies published by Wiley-VCH GmbH
exhibit a deep blue color in their reduced state. In contrast to that, for example Prussian blue (iron(III) hexacyanoferrate(II), Fe₄[Fe(CN)]₆), PB) is blue in its partly oxidized mixed-valence state and turns completely colorless upon reduction to Prussian white (PW). At best, the joint properties of PEDOT and PB electrodes lead to improved optical properties, for example, a higher visible light transmission change. However, the interplay of switching characteristics and charge balance of the EC half-cells increase the complexity of the system, which has to be considered as well. In Table 1, a comprehensive overview of a WO₃/PB and the most relevant PEDOT/PB ECDs is given. Ho et al. published a survey of tungsten oxide-based ECDs, where an ECD comprising complementary switching WO₃ and PB electrodes was reported (11.5 × 15.5 cm² active area). The device under investigation reached a contrast ratio (CR) of 18.3 (at 550 nm) and a coloration efficiency of 75 cm² C⁻¹ (at 550 nm).

2. Results and Discussion

2.1. Electrochemical Properties

In Figure 1a, the schematic representation of the complementary switching PEDOT-EthC₆/PB ECDs under study is given. The active EC materials are sandwiched between two commercially available ITO-coated (100 nm) PET films (127 µm) that serve as transparent conductive electrodes. The upper EC layer is an approx. 400 nm thick PEDOT-EthC₆ polymer coating (half-cell 1), while the lower EC layer is a PB thin film of approx. 100 nm thickness (half-cell 2). These two half-cells are separated by a UV-cured polymer electrolyte with a thickness of approx. 80 µm. Since the vertical dimensions of the PET substrates and the polymer electrolyte considerably differ from those of the EC films and the ITO layers, in Figure 1b, a scanning electron microscope image of a complementary PEDOT-EthC₆/PB ECD reveals a bimodal depth of the EC layer. This can be attributed to a density gradient of the EC coating as well as the different vertical dimensions of PET (127 µm) and ITO (100 µm) substrates. The PEDOT-EthC₆/PB ECDs under study show high optical contrast for the complementary switching ECDs with high optical contrast and short response time. The EC materials were deposited by large-area R2R processing on flexible PET-ITO films. The excellent functionality of sheet-to-sheet (S2S) processed flexible ECDs made from the roll-coated materials was demonstrated throughout 1 000 switching cycles. The S2S assembly of the EC device in the lab was subsequently transferred to a continuous and large-scale R2R laminating process, resulting in the first R2R-based electrochromic film device (50 × 100 cm²) completely fabricated by means of R2R processes.
microscopy (SEM) overview cross-section image is shown for clarification with two cutouts taken at higher magnification. The ITO layers on the PET substrates appear highly uniform with a well-defined interface. The PEDOT-EthC6 layer has a granular substructure and its boundary surface to the subjacent polymer electrolyte has a more irregular shape. This profile is ascribed to the honeycomb structure of the PEDOT-EthC6 film reported previously.[7] A top-view image of the PEDOT-EthC6 surface is shown in Figure S5a, Supporting Information. It is expected that the increased surface area due to the structuring of the EC layers accelerates the ion insertion and expelling processes during the color change of the EC thin films.[20–22] The nanoparticulate PB layer exhibits comparable structural features shown in Figure S5b, Supporting Information. The apparent gap between the EC layers and the electrolyte layer is presumably due to SEM sample preparation and thereby arising locally increased temperatures and shear forces. However, in wide-ranging SEM investigations, the multilayer assembly appears homogeneous and free of defects. In addition, the high uniformity is supported by the low haze values of the large-area ECDs (below 2%) in both the bleached and colored state. This means that only very little light is scattered at a wide angle or diffused due to macroscopic irregularities or rough interfaces in between the ECD layers, which points out the high transparency of the ECDs.

Another important component of an ECD, in addition to the half-cells from which it is composed, is the electrolyte that has to be tailored and optimized in terms of mechanical, chemical, and electrochemical properties for each EC system. In the present work, a UV-curable polymer (HQ674) based on polyethylene oxide with lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) as salt was used as electrolyte and separator.[23] The molecular weight of the HQ674 polymer is in the range of 8000–10 000 g mol$^{-1}$. Acrylate functional groups are introduced to the main chain in order to maintain a better mechanical strength of the polymer electrolyte thin films after coating and UV-curing. LiTFSI was used as the conducting salt to complex with the networked polymer. The ionic conductivity of the electrolyte polymer generally depends on the temperature resulting from macro- and micro-relaxations of the segmental movement of the polymer chains. Figure 2a shows the temperature dependence of the ionic conductivity for the HQ674 polymer electrolyte containing LiTFSI in an amount corresponding to an oxygen/lithium ratio of 30. The correlation of the ionic conductivity and temperature is almost linear, indicating the absence of crystalline domains in the electrolyte matrix. The ionic conductivity was found to be approx. $5.5 \times 10^{-5} \text{ S cm}^{-1}$ and $4.2 \times 10^{-4} \text{ S cm}^{-1}$ at temperatures of 30 °C and 70 °C, respectively. Figure 2b shows the thermogravimetry curve of the HQ674
polymer electrolyte. A thermal stability of up to approx. 280 °C was measured, making this electrolyte suitable for use in safe (no electrolyte leakage) all-solid-state ECDs.

The electrochemical properties of the ECDs were initially investigated by cyclic voltammetry (CV) at overall operation voltages between −1.4 V and 1.8 V with a scan rate of 10 mV s\(^{-1}\) (Figure 3a). During the anodic scan at voltages between −0.5 V and +1.2 V the course of the current suggests the superposition of two processes, namely the oxidation of PEDOT-EthC6 and the reduction of PB. The representative device is switched to the bleached state. Upon reversal of the voltage (cathodic scan), the respective back reactions set in at +1.1 V and are completed at −1.4 V. During this process, the device turns blue. The respective redox peaks are located at 0.3 V (anodic scan) and 0.2 V (cathodic scan). The substantial broadening of the redox peaks is a consequence of hindered diffusion in the electrolyte and insertion of the electrolyte ions from the polymer electrolyte into the EC layers\(^{[20–22]}\) as well as the superposition of the two signals of the two EC half-cells (see Figure S2, Supporting Information). The coulombic efficiency is close to 1, indicating completely reversible redox processes to occur. The CV results are in accordance with previously published data obtained from similar ECDs building on PEDOT and PEDOT derivatives.\(^{[7,8,17]}\)

The switching processes of the ECDs were further investigated in potentiostatic switching experiments between −1.4 V and 1.8 V as displayed in Figure 3b. The areal charge density, which corresponds to the area under the current curve, is calculated to be approx. 4.5 mC cm\(^{-2}\) (active area: 5 × 5 cm\(^2\)) for the initial cycles. The response time that is considered the time corresponding to a current drop to 10% of the starting (maximum) value amounts to 7 s for decoloration and 6 s for coloration. The response time of the ECDs is mainly limited by the sheet resistance of the ITO employed (approx. 50 Ω□\(^{-1}\)).\(^{[12]}\) The insulating properties of the PB layer have a certain, but comparably small effect.\(^{[16,24]}\) For similar PEDOT/PB devices (active area: 5 × 4 cm\(^2\), sheet resistance: approx. 50 Ω□\(^{-1}\)) Duluard et al. reported response times of more than 15 s for coloration. These systems, however, had a lower areal charge density of 1.2 mC cm\(^{-2}\), indicating faster kinetics for our PEDOT-EthC6/PB devices, as active area and sheet resistance of the conductive substrates are comparable.\(^{[12]}\)

Figure 4a displays the absorption spectra of the full PEDOT-EthC6/PB device in the dark and bleached states. All relevant electrochromic data of the PEDOT-EthC6/PB device and its single half-cells are displayed in Table 2. The dark state (−1.4 V) shows an intense deep blue color (\(L^* = 26.8, a^* = 12.8, b^* = −52.9\)) and a visible light transmission of 4%, whereas the bleached state (1.8 V) is distinguished by a highly transmissive, almost neutral tint (\(L^* = 77.9, a^* = −5.9, b^* = −0.6\)) and a visible light transmission of 53%. In the spectral range from 380 nm to 780 nm, an overall change of the lightness value \(ΔL^*\) of 51.1 takes place. The colored state is characterized by a strong and broad absorption band with a maximum at 630 nm. The transmission in the dark state at the maximum absorption...
wavelength is 0.5%. This signal is attributed to the individual absorption of the PEDOT-EthC6 film superposed with that of the PB thin film (the latter manifesting as shoulder at around approx. 690 nm). In the bleached state, the transmission at the maximum absorption wavelength is 46.7%, resulting in a contrast ratio CR of 93.4 and a (theoretical) coloration efficiency of 563 cm² C⁻¹ (assuming that the available charge density of the full cell is equal to the charge density of the half-cell with the lower charge density (PEDOT-EthC6: 3.5 mC cm⁻²)). Additionally, the individual contributions of the respective PEDOT-EthC6 and PB half-cells are given. The latter material only has a minor impact on the overall light transmission change of the device, however, in contrast to other commonly used counter electrodes (e.g. nickel oxide [2,4]), PB stands out due to its highly transparent, the low molecular weight, leading to improved interfacing with the electrodes (low interfacial resistance) and the ability of cross-linking (UV-curing) of the polymer electrolyte, which are maintained by the introduction to the use of an accordingly adjusted solid polymer electrolyte in terms of contrast ratio and neutral-colored bleached state of resistance) and the ability of cross-linking (UV-curing) of the main chain of the electrolyte polymer. The excellent ionic dissociation is due to the low lattice energy and the therefore highly dissociative character of the LiTFSI salt. Further advantages are the high transparency, the low molecular weight, leading to improved interfacing with the electrodes (low interfacial resistance) and the ability of cross-linking (UV-curing) of the electrolyte polymer after device lamination, thus establishing good electrode/electrolyte interfaces. The superior properties in terms of contrast ratio and neutral-colored bleached state of PEDOT-EthC6 compared to non-modified PEDOT is herewith also evident for the PEDOT-EthC6/PB and PEDOT/PB ECDs. In Table 1 we included a non-modified PEDOT/PB device as a state-of-the-art device for comparison, as published by Duluard et al. The flexible ECD based on in situ polymerized, non-modified PEDOT and PB offers a maximum contrast ratio of approx. 11.5 (at 650 nm) and a coloration efficiency of 380 cm² C⁻¹ (at 650 nm). The ECD comprising PEDOT-EthC6 presented here, shows a maximum contrast ratio of approx. 93.4 (at 630 nm) and a coloration efficiency of 563 cm² C⁻¹ (at 630 nm).

For practical applications, it is crucial that the ECDs show a performance constant in time over many cycles of operation. Unfortunately, there are not many scientific publications focusing on long-term cycling stability and EC materials are sometimes described as stable, although parameters such as light transmission change or charge capacity show a drop over the course of several thousand cycles. Barbosa et al. gave account of 180 switching cycles for a PEDOT/PB-based electrochromic system. They observed an exponential decay in the absorption change by 65%.[18] Other ECDs based on PEDOT and PB were operated more than 50 000 times by Tung et al. resulting in a decrease of the light transmission change from 50% to 27%.[27] The PEDOT-EthC6/PB ECDs investigated in the present publication were potentiostatically switched between −1.4 V (dark state) and 1.8 V (bleached state) and a transmittance change of 65%. Other ECDs based on PEDOT and PB were operated more than 50 000 times by Tung et al. resulting in a decrease of the light transmission change from 50% to 27%.[27] The PEDOT-EthC6/PB ECDs investigated in the present publication were potentiostatically switched between −1.4 V (dark state) and 1.8 V (bleached state). Both voltage steps were held for 60 s. This process was repeated 10 000 times, which resulted in a measurement time of approximately 14 days. The results in Figure 5 indicate a reversible redox behavior with a drop in charge density of approx. 1.3 mC cm⁻² within the first 1000 cycles that can be attributed to formation processes taking place in the device and, presumably, further electrochemical polymerization of the PEDOT-EthC6 polymer chain. The additional loss in charge density can be explained by hindered diffusion in the electrolyte and insertion of electrolyte ions from the polymer electrolyte into the EC layers during the accelerated cycling experiment.[27] Within the period from cycle 1000 to 10 000, the charge density remains remarkably stable. The maximum current during decoloration and coloration decreased from 22 mA (10 000th cycle) to 17 mA (10 000th cycle) and from 29 mA (1000th cycle) to 22 mA (10 000th cycle), as shown in Figure 5a. The response time remains constant at 7 s for decoloration and 6 s for coloration.

### Table 2. Electrochromic properties of the PEDOT-EthC6 and Prussian blue (PB) half-cells and the resulting ECDs (PEDOT-EthC6/PB, 5 x 5 cm²).

| Half-Cells      | Charge Density (mC cm⁻²) | Maximum absorption wavelength (nm) | Operating potential vs Li/Li⁺ | Color values (V) | Visible light transmission | Transmission at maximum operating voltage | Contrast ratio | Coloration efficiency (cm² C⁻¹) |
|-----------------|--------------------------|------------------------------------|-----------------------------|-----------------|---------------------------|------------------------------------------|--------------|----------------------------------|
| PEDOT-EthC6     | 3.5                      | 626                                | 2.1                         | 29.7| 17.0| 58.2| 4.4| 0.8| 71.9| 79.1| 530 |
| PB              | 4.5                      | 683                                | 3.6                         | 85.9| 13.0| 13.7| 65.5| 41.9| 2.3| 78 |
| Full cell 5 x 5 cm² | (3.5)a) 630 | Operating voltage Vₗₜₜ | −1.4| 26.8| 12.8| 52.9| 3.7| 0.5| 93.4| (563) |

*aAssumption that available charge density of the full cell is equal to the charge density of the half-cell with lower charge density (theoretical value).
(see Figure S3, Supporting Information). The same is valid for the charge density which decreases from 3.2 mC cm$^{-2}$ to 3.0 mC cm$^{-2}$ for the decoloring process and from 3.1 mC cm$^{-2}$ to 3.0 mC cm$^{-2}$ for the coloring process between cycle 1000 and cycle 10 000 (see Figure S3, Supporting Information). This corresponds to a respective charge retention of 94% and 97%, respectively (Figure 5b).

From the practical point of view, changes in the optical performance of the devices are more important than their electrochemical aging behavior. In Figure 6a, the absorption spectra of an ECD after 10 000 operations is compared to its pristine performance. The visible light transmission changes from 3%/50% to 2%/50% (dark/bleached state). The homogeneity of the devices after cycling is demonstrated by photographs in Figure 6b. The results from the electrochemical durability investigation over the course of 10 000 switching cycles show a drop in areal charge density. However, both response time and visible light transmission change remain roughly constant during the test. Consequently, the observed drop in charge density does not correspond to a degradation of the EC films themselves. In fact, the areal charge density of the PEDOT-EthC6 half-cell is approx. 3.5 mC cm$^{-2}$, while, for practical reasons, the areal charge density of the PB half-cell has been set to approx. 4.5 mC cm$^{-2}$ (see Figure S4, Supporting Information). The capacity of the full device should not exceed the capacity of the PEDOT-EthC6 half-cell, provided no side reactions occur. Therefore, during the formation (approx. 1000 cycles), the device levels off to its actual charge density. The fact that the optical properties, that is, the visible light transmission and colors remain almost constant over the course of 10 000 cycles underlines this argument. The visible light transmission changes are accompanied by a small loss in areal charge density, Duluard et al. reported a similar PEDOT/PB device showing a formation period over the first 200 cycles and losses in areal charge density and absorption change of 3% and 15%, respectively, between cycle 200 and cycle 1000.[12]

In fundamental research on the laboratory scale, many new ECPs and device configurations related therewith have been developed in the last decade.[11] Going beyond this academic level, it is highly challenging to transfer results from the lab to pilot or even industrial production. The ECDs described here were scaled-up to a size of 45 x 65 cm$^2$ (active area) by means of a customized sheet-to-sheet (S2S) laminating process established in a dry room (100 ppm H$_2$O). In an initial step, PEDOT-EthC6 (half-cell 1) and PB (half-cell 2) were separately deposited onto PET-ITO roll material by means of slot-die coating and drying at 120 °C and 100 °C, respectively.[7] In a second R2R process, the PEDOT-EthC6 films (half-cell 1) were rinsed in reservoirs successively filled with alcoholic solvent mixtures and subsequently dried at 100 °C.[7] In a last step, the two half-cells were S2S laminated by means of the HQ674 polymer electrolyte to obtain the final ECDs. Therefore, the viscous electrolyte resin was deposited onto half-cell 1 by doctor blade coating.
(coating width: 45 cm) under dry air atmosphere (dry room, 100 ppm H₂O). Subsequently, the second half-cell was laminated under slight pressure (calendaring roller) on top of the wet electrolyte layer that underwent curing by UV irradiation afterwards. Finally, the ECDs were fitted with copper tape bus bars, packed and sealed. Figure 7 shows a schematic drawing of the S2S device lamination along with photographs taken at the individual steps. With regard to the manufacturing process (S2S or R2R), possibly on an industrial scale, the consideration of environmental aspects and green chemistry metrics is also important. For the production of the electrochromic materials, ethanol and butanol (for PEDOT-EthC6) as well as water (for PB) are required. The use of water and alcohols provides a good starting point for the large-scale production of the ECDs, especially with regard to the processing of other ECPs, which are commonly processed with much more harmful solvents like chloroform or methanol.[10]

Figure 8 shows the in situ spectroelectrochemical characterization at five different measuring points along the longitudinal axis and photographic images of the large-area ECDs (45 × 65 cm²). The dark state (−1.4 V) shows the intense deep blue color (L* = 33.8, a* = 2.6, b* = −48.1) and a visible light transmission of 6%, whereas the bleached state (1.8 V) shows again a visible light transmission of 53% and an almost neutral tint (L* = 78.2, a* = −5.2, b* = −2.7). This results in a change of the lightness value ΔL* = 44.4. The results from the large-area device differ only slightly from the results of the small devices. The spectra taken at the different measuring points (Figure 8a) overlap in both the dark and bleached state almost perfectly. Homogeneity during the switching process (coloration/decoloration) is illustrated in Figure 9. A so-called “curtain effect” can be observed due to the ohmic drop resulting from the high sheet resistance of the PET-ITO used as conductive substrate. The response time for the large ECDs (45 × 65 cm²) is approx. 45 s for coloring and bleaching.

In anticipation of further scaling and going to pilot production, it was eventually elaborated on transferring the S2S device assembly batch process to a continuous R2R lamination process. First attempts to fabricate complete R2R processed continuous ECDs as a proof-of-concept experiment were successful. Half-cell 1 and 2 with a coating width of 50 cm were laminated and then cut into sheets of 100 cm length (Figure 10). Lamination and back-end assembly can be performed under special atmospheric conditions, for example, at lower humidity levels or under inert atmospheres, by means of housing or laminar flow arrangements. However, real application scenarios might demand the ECDs to be operated under ambient conditions, which means the influence of oxygen and humidity has to be considered during the entire life cycle. Our ongoing research addresses these factors and possible failure mechanisms. These results will be published elsewhere.

Figure 7. Schematic representation and photographic images of large-area processing of flexible ECDs (PEDOT-EthC6/PB) including electrolyte application in (a,c) and half-cell lamination (b,d). The width of the coated polymer films is 50 cm, resulting in ECDs with an active (switchable) area of 45 × 65 cm².

Figure 8. a) Absorption spectra and b) photographs of the ECD with an active (switchable) area of 45 x 65 cm². The photographic images include the measuring positions (1–5) of the colored (−1.4 V, bottom) and bleached (1.8 V, top) device.
3. Conclusion

Flexible ECDs based on a novel PEDOT-EthC6 polymer on PET-ITO as the cathodically-coloring working electrode, Prussian blue on PET-ITO as an anodically-coloring counter electrode, and a solid polymer electrolyte, show enhanced EC properties in terms of coloration efficiency, optical contrast, transmission and color neutrality in the bleached state, and cycling stability (10 000 switching cycles). The ECD fabrication was scaled-up to a maximum size of 45 × 65 cm² (active area) via a customized large-area S2S lamination process. The characterization of those multilayer assemblies demonstrates their visual uniformity and excellent functionality. The final device assembly was transferred to a continuous large-area R2R lamination process. The unique materials used for these ECDs in conjunction with the large-scale customized processing provide excellent prospects for the commercialization of high quality and flexible see-through ECDs.

4. Experimental Section

Commercially available PET-ITO films from Eastman Chemical Company (Flexvue OC50, sheet resistance: approx. 50 Ω□−1) were used as transparent conductive substrates. All reagents were purchased from Sigma–Aldrich and used without further purification unless otherwise noted. Electrochromic devices (lab samples: 5 × 5 cm², assembled in an argon filled glove box and prototype samples: 45 × 65 cm², assembled in a dry room with 100 ppm H₂O) were assembled in a sandwich-like configuration with R2R produced sidechain-modified PEDOT thin films (PEDOT-EthC6, cathodically coloring) on PET-ITO as working electrodes and PB (anodically coloring) on PET ITO as complementary switching counter electrodes. The manufacturing of the sidechain-modified PEDOT-EthC6 and PB thin films on PET-ITO is described elsewhere.[7,25] A solid polymer electrolyte (HQ674) based on polyethylene oxide, developed by Hydro–Québec, with LiTFSI as salt, was used as electrolyte and separator in the devices.[23] The polymer is obtained from a random alkylene oxide copolymer, which is synthesized by a ring opening polymerization of ethylene oxide and propylene oxide. The molecular weight of the HQ674 polymer is in the range of 8000–10 000 g mol⁻¹. The ionic conductivity of the polymer electrolyte was determined by electrochemical impedance...
spectroscopy using a Biologic VMP3 multi-channel potentiostat/galvanostat. The polymer electrolyte films were cut into disks with a diameter of 10 mm, sandwiched between stainless steel electrodes (SUS 304) and subjected to the impedance analyzer. The thermal stability of the HQ674 polymer electrolyte was investigated by thermogravimetry (TG) under nitrogen gas flow with temperatures ranging from 30 °C to 500 °C and a scan rate of 5 °C min⁻¹. The film thicknesses of the active layers in the devices were determined by means of a field emission scanning electron microscope Ultra 55 from Carl Zeiss. The appropriate parameters are given with the corresponding images. A Solartron 1260B electrochemical interface was used to study the cycling stability, electrochromism, flexible electrochromic devices, PEDOT, Prussian blue (PBS), colorimetric (CIELAB color space, with L° (lightness from black to white (0-100)), a° (negative values indicate green, positive values indicate magenta) and b° (negative values indicate blue, positive values indicate yellow) and in operando (in situ) spectroelectrochemical characterization of the devices were conducted using an Avantes AvaSpec-2048 standard fiber optic spectrometer combined with a balanced deuterium-halogen light source. UV–vis spectra were recorded in situ during potentiostatic switching of the device at room temperature under an inert atmosphere (glovebox).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was supported by the European Union’s Seventh Framework Program (FP7) under grant agreement no. 604204 (EELICON) and the Bavarian State Ministry of Economic Affairs and Media, Energy and Technology (Fraunhofer R&D Center for Electromobility). The authors would like to express their deep gratitude to COC Ltd. (Centrum Organické Chemie s.r.o., Rybitvi), Czech Republic, for the supply of the precursor compounds used in this study. Furthermore, the authors would like to thank Matteo M. Salamone for assisting in device assembly during the dry room trials at Hydro-Québec. S.M. consented to his photo being published in Figure 10. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
cycling stability, electrochromism, flexible electrochromic devices, PEDOT, Prussian blue

Received: August 24, 2020
Revised: October 22, 2020
Published online: December 10, 2020

[1] a) S. D. Rezaei, S. Shannigrahi, S. Ramakrishna, Sol. Energy Mater. Sol. Cells 2017, 159, 26; b) W. J. Hee, M. A. Alghoul, B. Bakhtyar, O. Elayebe, M. A. Shameri, M. S. Alrubaih, K. Sopian, Renewable Sust. Energy Rev. 2015, 42, 323.
[2] C. G. Granqvist, E. Avendaño, A. Azens, Thin Solid Films 2003, 442, 201.
[3] D. R. Rosseinsky, R. J. Mortimer, Adv. Mater. 2001, 13, 783.
[4] a) C. G. Granqvist, M. A. Arvizu, I. Bayrak Pehlivan, H.-Y. Qu, R.-T. Wen, G. A. Niklasson, Electrochim. Acta 2018, 259, 1170; b) A. Cannavale, U. Ayr, F. Fiorito, F. Martellotta, Energies 2020, 13, 149; c) Y. Ke, J. Chen, G. Lin, S. Wang, Y. Zhou, J. Yin, P. S. Lee, Yi Long, Adv. Energy Mater. 2019, 9, 1900266; d) A. L.-S. Eh, A. W. M. Tan, X. Cheng, S. Magdassi, P. S. Lee, Energy Technol. 2018, 6, 33; e) J. Jensen, M. Hösel, A. L. Dyer, F. C. Krebs, Adv. Funct. Mater. 2015, 25, 2073.
[5] R. D. Rauh, Electrochim. Acta 1999, 44, 3165.
[6] L. Groenendaal, G. Zotti, P.-H. Aubert, S. M. Waybright, J. R. Reynolds, Adv. Mater. 2003, 15, 855.
[7] S. Macher, M. Schott, M. Sassi, I. Facchinetti, R. Ruffo, G. Patriarca, L. Beverina, U. Posset, G. A. Griffin, P. Löbmann, Adv. Funct. Mater. 2020, 30, 1906254.
[8] S. Duluard, B. Ouvrard, A. Celik-Cochet, G. Campet, U. Posset, G. Schottner, M.-H. Delville, J. of Phys. Chem. B 2010, 114, 7445.
[9] R. Ruffo, A. Celik-Cochet, U. Posset, C. M. Mari, G. Schottner, Sol. Energy Mater. Sol. Cells 2008, 92, 140.
[10] a) A. M. Österholm, D. E. Shen, D. S. Gottfried, J. R. Reynolds, Adv. Mater. Technol. 2016, 1, 1600063; b) J. A. Kerszulis, K. E. Johnson, M. Kuepferl, D. Khoshabo, A. L. Dyer, J. R. Reynolds, J. Mater. Chem. C 2015, 3, 3211; c) L. Beverina, G. A. Pagani, M. Sassi, Chem. Commun. 2014, 50, 5413; d) M. Sassi, M. M. Salamone, R. Ruffo, C. M. Mari, G. A. Pagani, L. Beverina, Adv. Mater. 2012, 24, 2004; e) M. Sassi, M. M. Salamone, R. Ruffo, G. E. Patriarca, C. M. Mari, G. A. Pagani, U. Posset, L. Beverina, Adv. Mater. 2016, 26, 5240.
[11] P. M. Beaujuge, J. R. Reynolds, Chem. Rev. 2010, 110, 268.
[12] S. Duluard, A. Celik-Cochet, I. Saadeddin, A. Labouret, G. Campet, G. Schottner, U. Posset, M.-H. Delville, New J. Chem. 2011, 35, 2314.
[13] D. Eric Shen, A. M. Österholm, J. R. Reynolds, J. Mater. Chem. C 2015, 3, 9775.
[14] K.-C. Ho, T. G. Rukavina, C. B. Greenberg, J. Electrochem. Soc. 1994, 141, 2061.
[15] D. R. Rosseinsky, L. Glasser, H. D. B. Jenkins, J. Am. Chem. Soc. 2004, 126, 10472.
[16] M. J. Piernas Munoz, E. Castillo Martinez, Prussian Blue Based Batteries, Springer Nature, Cham, Switzerland 2018.
[17] T.-S. Tung, K.-C. Ho, Sol. Energy Mater. Sol. Cells 2006, 90, 521.
[18] P. C. Barbosa, L. C. Rodrigues, M. M. Silva, M. J. Smith, A. J. Parola, F. Pina, C. Pinheiro, Electrochim. Acta 2010, 55, 1495.
[19] C. M. Lampert, A. Agrawal, C. Baertlien, J. Nagai, Sol. Energy Mater. Sol. Cells 1999, 56, 449.
[20] A. Zeng, E. Liu, I. F. Annengren, S. N. Tan, S. Zhang, P. Hing, J. Gao, Diamond Relat. Mater. 2002, 11, 160.
[21] K. Jüttner, W. J. Lorenz, Mater. Sci. Forum 1989, 44–45, 191.
[22] K. Jüttner, W. J. Lorenz, W. Paatsch, Corros. Sci. 1989, 29, 279.
[23] European Patent Application EP 2 570 846 A1: Flexible transparent electrochromic device, 20.03.2013.
[24] a) J. C. Woidel, I. De P. R. Moreira, S. T. Bromley, F. Illas, J. Mater. Chem. C 2009, 19, 2032; b) J. Agruiselas, J. J. García-Jareño, D. Gimenez-Romero, F. Vicente, J. Phys. Chem. C 2009, 113, 8438.
[25] A. Gotoh, H. Uchida, M. Ishizaki, T. Satoh, S. Kaga, S. Okamoto, M. Ohta, M. Sakamoto, T. Kawamoto, H. Tanaka, M. Tokumoto, S. Har, H. Shiozaki, M. Yamada, M. Miyake, M. Kurihara, Nanotechnology 2007, 18, 345609.