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Development and Manufacture of Polymer-Based Electrochromic Devices

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The field of organic electrochromics is reviewed here, with particular focus on how the "electrochromic" as a functional material can be brought from the current level of accurate laboratory synthesis and characterization to the device and application level through a number of suited roll-to-roll methods compatible with upscaling and manufacture. The successful approaches to operational devices are presented in detail, as well as areas where future research would have a high impact and accelerate the development such as highly conducting and transparent substrates, electrolytes adapted for multi-layer application and morphologically stable conjugated polymers.

1. Introduction

Electrochromism—the alteration of absorption/color by electrochemically induced redox reactions—is a property shared by several electroactive species including inorganic transition metal oxides (e.g., WO_3, IrO_2, MoO_3), hexacyanometallates ($[Fe^{III}Fe^{II}(CN)_6]^-$), viologens (bipyridilium compounds) and conjugated polymers.[1–9] Electrochromic compounds were at first expected to find applications in devices for information displays (clocks, calculators, screens etc.), but interest faded as liquid crystal displays conquered the market, conceivably due to faster switching and facile mass scale production. Even so, electrochromic technologies are facing a brighter future due to renewed interest in consumer products integrating EC technology in addition to the promising results reported by several research laboratories. A prominent example of an EC application is found in Boeing's 787 Dreamliner airplane where the manually operated window blinds has been substituted by EC technology allowing the passenger to block out sunlight by pushing a button.[10] Another EC application is in car rear view mirrors, where an electrochromic system comprising thiazines and viologens deposited on a polished alloy attenuate the headlight glare of cars coming from behind.[10,11] Pioneering the field of commercial EC devices are oxides of the transition metal (most notably WO_3) that find applications in corporate buildings as dimmable windows, also known as smart windows.[12–14] Beside the architectural finesse in substituting dimmable windows for curtains or blinds, significant reductions in energy consumption due to effective management of solar irradiation have been shown.[13,15] These energy savings are intrinsically economically beneficial, and in an age of increasing climate awareness, development of EC technologies could benefit from the interest in energy savings in connection with reduction of greenhouse gas emissions.

Compared to the focus on materials development and characterization, research in electrochromic polymer (ECP) based devices has so far been rather limited. Although the majority of literature on ECP synthesis includes examples of electrochemical switching thin films, it is rarely in the form of functional devices and most often in the form of a thin coated film submerged in a liquid electrolyte bath, thus far from any conceivable application. In the few cases that approach the proof-of-concept level, in-depth device analyses are seldom provided. While achievements in ECP development are inherently important and should by no means be depreciated, the field of polymer electrochromics is now at a point where state-of-the art ECPs with excellent properties in controlled laboratory settings are not tested further in regular device settings, thus never realizing any commercial potential. To address this ambiguity, this report highlights many aspects of device fabrication and provides examples of how the challenges encountered in developing polymer based electrochromic devices (ECDs) are targeted. By assuming a device perspective we hope to bring together researchers within polymer electrochromics and fuel renewed interest in device development. To gain the most of this review, the authors recommend the reader to familiarize him/herself with the vast body of literature on ECP synthesis and characterization. Among the many groups that have contributed to the progress and refinement of ECPs, the work of the Reynolds group stand out.[16–38] The completion of the color circle using solution processable ECPs was a major accomplishment; not the least from a manufacturing perspective.[7,8] While the Reynolds group utilizes a propylene dioxythiophene (ProDOT) unit in several of their polymers, the Wudl group reported on (poly) thieno-substituted thienopyrazines as the electrochromic system.[39–41] Other notable contributions come from the group of Wu relying on polyoctylcyclopentadithiophenes

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for electrochromic switching,[42,43] and the group of Cihaner who also employs ProDOTs.[44,45] The Toppare group is recognized for their work primarily on electrochemically synthesized ECPs, while Bendikov and co-workers published an electrochemically synthesized selenoderivative of PEDOT.[9,46] The above list is by no means exhaustive in terms of the amount of published research, but serves as a good starting point for readers not familiar with ECP development. For general information about ECP design, donor–acceptor approach and working mechanism the reader is directed to the work of Beajuge et al.,[47,48] Heinze,[49] Yashima et al.,[50] and Mortimer.[51,52] Two excellent textbooks by Mortimer, Monk and Rosseinsky are available and should be considered mandatory reading.[11,53] The reader is directed to reviews on various aspects of organic electrochromic polymers and devices,[9,51,52,54–57] as well as on transition metal electrochromics.[1–3]

2. Electrochromic Device Features

2.1. Optical Contrast

The difference in transmittance between the two redox states of an ECD (usually the colored and the bleached state) is referred to as the optical contrast, or ΔT. The optical contrast is of interest as it quantifies how well the electrochromic compound is turned "on" and "off". The optical contrast has traditionally been measured at the wavelength of the maximum absorbing peak (Abs_{max}) and reported relative to the applied potential, but reports using the photopic contrast, relative luminance (% Y) and color contrast (ΔE^*) are also employed to account for the eye response to stimuli.[20,58–60] It should be noted that although a high optical contrast is desirable, it does not necessarily equal an electrochromic transition from colored to colorless, as the optical contrast does not provide information on other parts of the spectrum than Abs_{max}. Though the intensity of the maximum absorbing peak is altered due to redox reactions, other parts of the spectrum may change, and tailings from the near infrared regions of the electromagnetic spectrum could disrupt complete bleaching.[19,25]

The components in ECDs intrinsically affect the overall transmission, which makes it worthwhile to acknowledge the different settings in which ECDs and ECPs are evaluated. Transmission measurements for ECPs are typically reported relative to a reference (e.g., a cuvette containing a blank substrate); hence optical contrast obtained this way provides information on the maximum contrast obtainable for the polymer. Electrochromic devices on the other hand, are not functional without electrode substrates, electrolyte and a charge balancing electroactive species (e.g., a second polymer) which influence the optical contrast as shown in **Figure 1**.

Glass is the least disruptive substrate, and a 1 mm thick glass substrate without electrode material reduces the practical transmittance by ≈10% (black trace); while indium-doped tin oxide (ITO, R_s app. 20 Ohm/sq) on glass further contributes to an additional 10% reduction (green trace). Flexible electrode substrates such as polyethylene terephthalate (PET, thickness 185 µm) coated with ITO (R_s app. 35 Ohm/sq) reduces the transmittance to roughly 75% (turquoise trace) and PET substrates (72 µm)

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Aubrey Dyer obtained her Ph.D. in Chemistry from the University of Florida in 2007 in the field of conjugated polymer-based electrochromics and light-emitting electrochemical cells. She was a Senior Research Scientist at the Georgia Institute of Technology from 2012 to 2014 working in the areas of conjugated polymers for electrochromic and charge storage applications. In August 2014 she moved to Clayton State University in Morrow, Georgia where she is currently Assistant Professor. Her research interests are in understanding electrochemical, charge transport, and optical properties of electroactive materials for electrochromic and charge storage applications.

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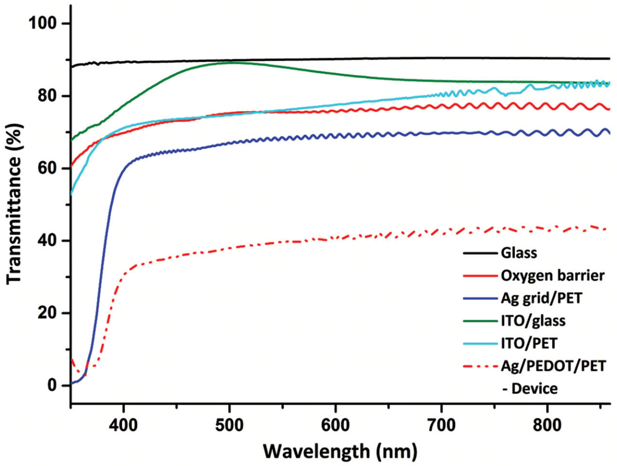

Figure 1. Transmittance for electrode substrates commonly used in ECDs. The traces show values for a single substrate measured in a transmission geometry with normal incidence.

containing a hexagonal silver grid leads to a 40% transmittance decrease (blue trace).[61] Barrier foils used to increase the photochemical stability of ECPs likewise absorb light, reducing the transmittance by approximately 30% (red trace).[62] These numbers are useful when comparing devices and polymers but one should note that the traces shown in Figure 1 are the transmission curves of a single sheet of substrate and ECDs comprise a front and back side and additional layers which decrease further the optical transmission of the device. The red dashed trace is an example of a device comprising two silver grid electrodes on PET, each coated with PEDOT and a PMMA/ionic liquid electrolyte. The relatively low transmittance of this device demonstrates the challenges associated with using flexible substrates for ECD-window materials as shown by several groups.[23,63–65] Another possible window electrode type for electrochromic devices is graphene that allows very high transparencies beyond 95% with the tradeoff of high sheet resistances (>1 kΩ/sq).[157]

2.2. Response Time

Sometimes referred to as switching speed, the response time is obtained by correlating the change in transmittance with time required for that change in response to an applied potential. The response time is of interest, since a change over a few minutes is suitable for appliances such as blinds, large area billboards, and so forth, while other devices require second or sub-second response (clocks, screens, etc.). The absence of a common protocol on how to report response time results in response times being reported differently amongst research groups as shown in **Table 1**. The smaller the change in transmittance, the faster is the electrochromic for a given device, which emphasizes comparison of a given response time to the optical contrast obtained. However to thoroughly report device response it does make sense to report on different levels of optical contrast, considering that the majority of the redox reactions occur in the beginning of a switch, for example, 90% of a full switch might occur in two seconds while the last 10% takes five seconds to complete. This is caused by the faster movement of charges and charge balancing ions when the electric field is first established, but as the charges move, the field is screened which limits the movement of charges and charge carriers.[66] Two notable observations are made when electrochemically switching ECDs. Initially the first 5–10 switches are usually quite slow and incomplete, but following this “break-in” the ECP films reach their maximum response time and optical contrast. This electrochemical improvement is most likely due to incorporation of solvent into the polymer film. Solvent molecules are inserted along with ions upon doping, and are necessary for free ion movement in and out of the film.[49,67] Secondly, the response time is generally shorter when reducing ECP films compared to oxidizing them, which is due to the doped state (the oxidized state/p-doped for most ECPs) is electrically conducting and this facilitates charge transport in the initial stages of reduction, contrary to the neutral insulating state.[66–68] In ECDs the response time is affected by several components, with the primary difference being the transport of charge balancing ions through a semisolid/solid polymer gel of poly(methyl methacrylate), poly(ethyleneoxide) or similar, as opposed to the low viscosity electrolytes (based on acetonitrile, propylene carbonate, etc.) employed in a standard three electrode set-up. The response time is dependent upon the ionic mobility, which in turn is affected by the electrolyte viscosity. This affects the interactions between the ions and the polymer chains, with the size of the ions and concentration of polymer as important factors.[68–71] Additionally, ECDs are comprised of two polymers (or electroactive species) reacting complementary to each other, whereby the slowest reaction will be rate limiting.

2.3. Memory Effect

The memory effect of an electrochromic compound or device is the ability to maintain a given redox state when taken to open circuit. In effect this allows the electrochromic window or display to maintain a color state without a continuous power supply; a feature that differentiates ECDs from other display technologies, such as OLEDs or LEECs that require a continuous supply of electrical energy to operate.[72,73] Depending on the application of the ECD, the color can be refreshed by a short potential pulse at certain intervals.[74,75] The memory effect stems from electrons being “trapped” in one redox state of the polymer which prevents them from reverting to the equilibrium state, when the device is taken to open circuit. A less stable redox state cannot be maintained indefinitely, and the memory effect can be regarded as the slow reaction of a polymer going from a less stable redox state to a more stable one in reacting with the surrounding chemical environment.[76] Since the memory effect is dependent on the chemical environment surrounding the electrochromic polymer film, it is not solely a materials property, and at least two factors influence the memory effect: First, ECDs are electrochemical cells with an electromotive force that depend on the equilibrium between the ECP and the counter species (e.g., the secondary polymer). In other words, the memory effect of a polymer is affected by the counter polymer, or more generally the counter species (in a device the counter electrode is another polymer, while in a three electrode set-up the counter electrode is usually of metal).

Table 1. Overview of selected polymer-based electrochromic devices. The table is not a complete account of every polymer based ECD, but an overview of reports mainly addressing device fabrication.

ECP 1 (Primary)	ECP 2 (Secondary)	Electrolyte[i]	Abs$_{max}$/color change[ii]	Optical contrast[iii]	Potential window[iv]	Response time[v]	Stability[vi]b>	Device size	Notes	Ref.
Poly(4,4′-dipentoxy-2,2′-bithiophene)	Poly(*N*,*N*′-dimethyl-2,2′-bipyrrole)	Hydrin C, $LiClO_4$ (solid)	620 nm	38%	+/– –0.55 V	Red/Ble 5	Δ*T* = 27% after 500 dps	15 mm × 17 mm	ECP blended w. Hydrin C	[117]
			Dark grey/light grey			Ox/Col 7.5				
Poly(4,4′-dipentoxy-2,2′-bithiophene)	Poly(-*o*-methoxy-aniline)-PTSA	CF_3COOH, TBAP, Acetonitril (liquid)	620 nm	56%	–1.15 V to +0.65 V	Red/Ble 1 s	Δ*T* = 33% after 300 dps	N.A.	ECP blended w. Hydrin C	[118]
			Yellow/blue			OX/Col 12 s			Deg. starts immediately	
PEDOT:PSS	Poly(pyrrole): Indigocarmine	Hydrin C, $LiClO_4$ (solid)	640 nm	52%	+/–1.5 V	Red/Ble 4 s	N.A.	15 mm × 17 mm	ECP blended w. Hydrin C	[119]
	Dodecylsulfate					Ox/Col 4 s				
PEDOT:PSS	Poly(-*o*-methoxy-aniline)-PTSA	Epichlormer-16, $LiClO_4$ (solid)	640 nm	75%	–0.8 V/ +0.9 V	Red/Col 20 s	Δ*T* = 42% after 100 dps	20 cm^2	ECP blended	[120]
			Yellow/blue			Ox/Ble 20 s				
Poly{3-[12-(p-methoxyphenoxy) Dodecyl]thiophene}	PEDOT:PSS	P(EO-EPI), $LiClO_4$ (solid)	650 nm	42%	0 V/+1.7 V	Red/Col 15 s	Δ*T* = 31% after 200 dps	1 cm^2	ECP blended	[155]
			Red/blue			Ox/Ble 6 s				
PEDOT	PEDOT	PEO, PC, $LiClO_4$ (swollen)	630 nm	33%	0 V/+1.2 V	Col 60 sec	Δ*T* = 31% after 1500 cycles	1 cm^2	Semi IPN	[128]
			Light blue/dark blue			Ble 30 s (90%)				
Poly(3,4-(2,2′-dimethylpropylene-dioxy)thiophene	Poly(3,4-(2,2′-dimethylpropylene-dioxy)thiophene	PEO,PC, $LiClO_4$ (swollen)	574 nm	32%	0 V/+1.2 V	Col (+1.2 V) sec	Δ*T* = 31% after 1500 cycles	6 cm^2	Semi IPN	[104]
						Ble 9 sec (0 V)				
						(80%)				
PEDOT	N.A.	PEGDA, PC, LiTfO (solid)	Blue/grey	45%	0 V/2 V	Red/col 4 s	N.A.	3.5 cm × 4 cm	Sem IPN	[102]
				Phot.C.		Ox/Ble 4 s			In situ	
Poly(bis[3,4-ethylenedioxythionyl]-thiophenedioctylsilane)	N.A.	PEGDA, PC, LiTfO (solid)	485 nm	24%	N.A.	0.5 to 1.2 s. average	N.A.	N.A.	Sem IPN	[103]
			Blue/red						In situ	
Poly(3-methyl-3,4-dihydro-2H-thieno[3,4b]dioxepin-3-yl) methylacrylate	N.A.	PEGDA, PC, LiTfO	555 nm	48%	+/– –2 V	Red/col 2 s	Phot.C. = 45%	5.8 cm^2	Sem IPN	[131]
		(solid)	Blue/grey	Phot.C		Ox/ble 1 s	After 10.000 cycles		In situ	

Continued

Table 1. Continued

ECP 1 (Primary)	ECP 2 (Secondary)	Electrolyte[i]	Abs$_{max}$/color change[ii]	Optical contrast[iii]	Potential window[iv]	Response time[v]	Stability[vi]b>	Device size	Notes	Ref.
Poly(3,4-(2,2′-dimethylpropylene-dioxy)thiophene	N.A.	PEGDA, PC, LiTfO (solid)	Blue/grey	46%	+/–2 V	R/col 1.8 s	N.A.	4 cm^2 (105 cm^2)	Sem IPN	[130]
						Ox/ble 3.5 s			In situ	
						(95%)				
				Phot.C						
Poly(3,4-(2,2′-dimethylpropylene-dioxy)thiophene	N.A.	PEGDA, PC, LiTFSI (solid)	575 nm	48%	(+/–2 V)	Red/col 2 s	N.A.	171 cm^2	Sem IPN	[129]
			Blue/grey	Phot.C		Ox/ble 6 s			In situ	
						(90%)				
PEDOT:PSS	PEDOT:PSS	PEO, LiTfO, THF	650 nm	15%	0/3 V	Col (3V) 16s	10% loss after 500 cycles	25 cm^2	Symmetrical	[63]
						Ble (0V) 20s			All polymer	
						(90%)				
			Dark blue/light blue							
PEDOT:PSS	PEDOT:PSS	[emim][Br]: poly[ViEtIm][Br]	650 nm	13%	0/3 V	N.A.	No loss after 30.000 cycles	1.5 cm^2	Symmetrical	[124]
		(gel)	Dark blue/light blue	(10–17%)					All polymer	
PEDOT	PEDOT	Poly ionic liquid	620 nm	22%	0/2.5 V	Col (2.5V) 3	No change after 1000 cycles	2 cm^2	Symmetrical	[125]
			Dark blue/light blue			Ble (0V) 3s				
						(90%)				
Poly(3,4-(2,2′-dimethylpropylene-dioxy)thiophene	PBEDOT-*N*-MeCz	PMMA, TBAPF$_6$, PC, ACN (semisolid gel)	540 nm	51%	+/– 1.5 V	Red/blue 8	NA	N.A.	All polymer	[23]
						Ox/green 8				
						(80%)				
			Blue/green							
poly((2,2-bis(2-ethylhexyloxymethyl)-propylene-1,3-dioxy)-3,4-thiophene-2,5-diyl)	PEDOT:PSS	PMMA, EMITFSI, ACN (semisolid gel)	550 nm	29%	–0.5 V/+1.0 V	Ox(ble) 0.3s	N.A.	1 cm^2	ITO free	[61]
			Magenta/light blue			Red (col) 2.5 s			Flexible	
Poly(3,4-(2,2′-dimethylpropylene-dioxy)thiophene	Au or C	PMMA, LiClO$_4$, PC, EC/GBL	580 nm	60%	+/– 1 V	1 s	50.000 cycles	3 inches ×3 inches	Ag ref. foil	[144]
			Dark blue/light blue			(% N.A.)				
poly (3–6-bis-(2-(3,4-ethylendioxy)thienyl)-N-methylcarbazole	PEDOT	PEG-DA/MA, PC, LiTrO	555 nm	30% Phot.C	–1 V/+1.4 V	Ox 1.5S col	90.000 cycles	30 cm^2	ITO/glass	[58]
		(solid)				Red 0.9 ble (90%)				

Continued

Table 1. Continued

ECP 1 (Primary)	ECP 2 (Secondary)	Electrolyte[i]	Abs$_{max}$/color change[ii]	Optical contrast[iii]	Potential window[iv]	Response time[v]	Stability[vi]b>	Device size	Notes	Ref.
poly((2,2-bis(2-ethylhexyloxymethyl)-propylene-1,3-dioxy)-3,4-thiophene-2,5-diyl)	poly(*N*-octadecyl- (propylene-1,3-dioxy)-3,4-pyrrole-2,5-diyl)	PMMA, PC, TBABF$_4$	540 nm	61%	–0.6 V/+1.6 V	Ox 60 s	NA	5 cm^2	ITO/glass	[112]
		(semisolid gel)	Magenta/colorless	(vs ref)		Red: NA (96%)				
poly(aniline-N-butyl -sulfonate) and poly{[1,3-bis(9,9′-dihe-xylfluoren-20-yl)azul- enyl]-alt-[2″,7″-(9″,9″-dihexylfluorenyl]}	PEDOT and poly(3-hexylthiophene)	TBAP, γ-butyrolactone (liquid)	470 nm, 515 nm, 600 nm, 710 nm	14–24%	–4 V/+2 V	Ox/ col 13.3 s	NA	4 cm^2	ITO/glass	[151]
			Light grey/black			Red /ble 7.1s (70%)			Multilayered device	
poly((2,2-bis(2-ethylhexyloxymethyl)-propylene-1,3-dioxy)-3,4-thiophene-2,5-diyl)	poly(*N*-octadecyl- (propylene-1,3-dioxy)-3,4-pyrrole-2,5-diyl)	PMMA, EMITFSI, ACN (semisolid gel)	548 nm	44%	+/– –2 V	Ox/ble	Δ*T* = 21% after AM1.5G, 1000 W/m^2, 45 °C), 100 h	10 cm^2	ECD powered by OPV	[75]
			Magenta/colorless			3.8				
				(vs ref)		Red/col 4.8				
poly((2,2-bis(2-ethylhexyloxymethyl)-propylene-1,3-dioxy)-3,4-thiophene-2,5-diyl)	poly(*N*-octadecyl- (propylene-1,3-dioxy)-3,4-pyrrole-2,5-diyl)	PMMA, LiBTI, PC (semisolid gel)	550 nm	20%	OPV: V_{OC}: 0.7 V; J_{SC}: 3 mA/cm^2	2–3 s	NA	1 cm^2	ECD powered by OPV	[137]
			Magenta/light blue							
Poly(3,4-(2,2′-diethyl propylene-dioxy)thio- phene	FL dye1,Br$^-$/Br^{3-}	Br$^-$/Br^{3-}, LiClO$_4$	620 nm	34%	DSSC: V_{OC}: 0.66 V; J_{SC}: 0.12 mA/cm^2	Ox/ble	NA	1 cm^2	ECD powered by DSSC	[141]
						96 sec				
						Red/col				
						36 s				
Poly(3,4-(2,2′-dimethyl propylene-dioxy)thio- phene	Ruthenium 535–4TBA, I$^-$/I^{3-}	LiI, I$_{2,}$ PC (liquid)	637 nm	38%	DSSC: V_{OC}: 0.66 V; J_{SC}: 2.92 mA/cm^2	Ox/ble 4 s	Δ*T* = 33% after 1500 cycles	4 cm^2	ECD powered by DSSC	[139]
			Blue/light red			Red/col 1 s				
poly((2,2-bis(2-ethylhexyloxymethyl)-propylene-1,3-dioxy)-3,4-thiophene-2,5-diyl)	poly(*N*-octadecyl- (propylene-1,3-dioxy)-3,4-pyrrole-2,5-diyl)	PMMA, PC, LiBTI (semisolid gel)	540 nm	60%	–0.5/+1.0 V	1.6 s	NA	1.6 cm^2	ECD powered by polymer capacitor	[140]
			Magenta/colorless	(vs ref)		(95%)				

[i] If described in the literature, the state of electrolyte is given.

[ii] The wavelength of the maximum absorbing peak and the color of the two redox states.

[iii] The difference in transmittance between the two redox states is usually referred to as the optical contrast. The difference in transmittance is in some instances reported as photopic contrast (phot. C). Not all authors state whether or not the contrast is obtained relative to a reference.

[iv] The lowest and highest potential applied to the device during switching.

[v] The time required to obtain a percentage of the full transmittance change at the maximum absorbing peak. There is no standard percentage used for reporting response times, but 95% of the full electrochromic switch is commonly used. Where reported the percentage is given in parenthesis. It is also stated if the device bleaches (ble) or colors (col) by oxidation (ox) or reduction (red).

[vi] Not reports contain stability measurement and it is reported differently between research groups.

Secondly, as the electrochemical reaction is hindered due to open circuit, charge carriers in the electrolyte layer is the sole option for the reversible redox reaction, and the diffusion of these charge carriers is affected by electrolyte composition, viscosity and thickness.

2.4. Coloration Efficiency

The number of color centers formed as a function of the charge used to bring about this change is described by the coloration efficiency (sometimes denoted as the electrochromic efficiency), η, usually represented in cm^2 C^{-1} (area per charge) and given by:

$$\eta = (\log(\%T_1 / \%T_2)) / (Q)$$

where$\%T_1$ and $\%T_2$ refer to the transmission before and after redox switching respectively and Q is the charge consumed per area. In ECDs, high coloration efficiency is desirable for the primary ECP, while low values are advantageous for the charge balancing polymer. Coloration efficiencies are reported in several ways, and have so far been regarded as a materials property.[11,21,24] However, the device coloration efficiency ($(\eta_\mathrm{d} = \eta \mathrm{w})$) was recently proposed as an alternative way of relating the number of color centers formed to the consumed charge per area in a particular device setting.[61] η_d is related to η by the device correction factor w, which includes contributions from electrode materials, electrolyte matrix and Faradaic side reactions occurring in the device. η_d can be used to compare devices with identical polymers, thereby being a useful tool for evaluating a particular device setting (e.g., electrolyte composition or electrode substrate). Likewise η_d should prove useful when designing electronic circuitry for devices.

3. Device Manufacture

3.1. Coating and Printing Techniques

Electrochromic devices based on solution processable polymers enable the utilization of printing and coating methods for processing of the functional layers. In order to be processable from organic solvents, the polymer backbone needs to contain solubilizing alkyl or alkoxy side chains. Common to all solution-based deposition methods is the dissolution of the polymer in an appropriate solvent, deposition onto a substrate, and evaporation of the solvent whereby a thin solid polymer film is formed.[47,77,78]

Spin coating is a simple technique that is fast and easy to use with relatively simple equipment requirements.[79] For deposition by spin coating the substrate is placed on the spincoater and held in place by a vacuum. The polymer solution is applied while the substrate spins or prior to this. Centrifugal forces push the solution to the edges of the substrate, whereby a wet polymer film is formed, followed by evaporation resulting in a thin solid film. An advantage of spin coating is that the results are highly reproducible, yielding films of identical thickness and morphology. These advantages make spin coating an excellent technique for small-scale laboratory experiments. The disadvantage is that large amount of material is wasted in the process, making spin coating material inefficient and unsuitable for large-scale production or simple EC displays that require pattering of some of the layers.

Of particular interest for ECs are screen printing, inkjet printing, flexographic printing, bar and blade coating, slot-die, and spray coating, as illustrated in **Figure 2**. Printing methods allow additive processing and direct patterning of electrodes or electrochromic layers, while coating technologies are large area deposition methods without specific patterning possibilities beside shadow masking or coarse stripes. Therefore additional post-patterning processes such as lithography, dry and wet etching, and photopatterning are often required.[80,81]

Screen printing is based on a mesh with open and closed areas defining the fixed printing motif. The ink is forced through the open areas using a squeegee moving off the screen mesh. Generally the printing paste is of high viscosity with thixotropic behavior. Flatbed screen printing is ideal for sheet-to-sheet processing and small sale processes while rotary screen printing allows increased output in an industrialized R2R based environment. Rotary screen printing of electrolyte with a conductive squeegee has been successfully used for the patterning of pre-coated PEDOT:PSS by electrochemical over-oxidation.[82] Screen printed electrolyte has also been used for the fabrication of an all-organic active matrix display.[83] Additive processing of PEDOT and V_2O_5 electrodes in form of stripes and checkerboards has been carried out to fabricate solid state EC devices.[84] Traditionally, the method is also used for the deposition of electrode structure for electrical connection and circuitry in EC devices.[75,85]

Inkjet printing is a drop-on-demand printing technique where the digital printing motif can be changed instantaneously. Typically the drop formation is induced through piezo actuators and specific electrical voltage waveforms inside the printing head that contains ink chambers and nozzle orifices. The inkjet parameters and printing ink of low viscosity needs fine-tuning to allow precise film formation and print quality. The method was used to fabricate ITO-free EC devices with inkjet-printed WO_3 nanoparticles to show static information

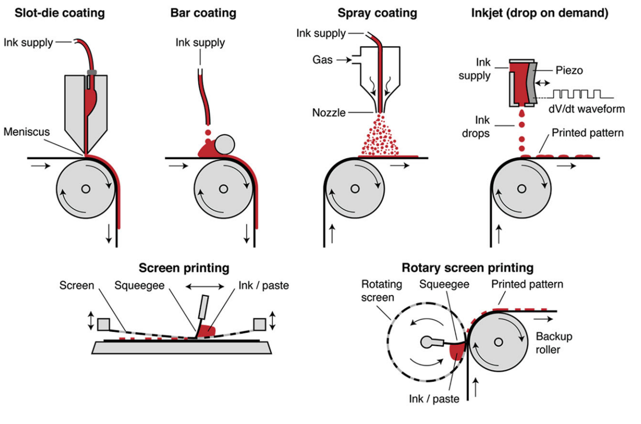

Figure 2. Overview of commonly used printing and coating methods in the fabrication of EC devices. Adapted with permission.[56] Copyright 2012, John Wiley and Sons Ltd.

such as text and numbers.[86] Multiple inkjet prints of PEDOT:PSS, epoxy resin, silver, and supporting hydrophobic polystyrene ink has also been employed to build a flexible active matrix display on PET foil.[87] A solid state EC device with patterned electrodes formed from water-based vanadium oxide gel could be assembled while the lithium-based polymer electrolyte was homogeneously spread between the electrodes.[88] Similar procedures were used to print patterns of PANI-silica and PEDOT-silica colloidal composite particles as electrochromic layer on ITO-PET film.[89] Good electrochromic behavior with color switching between yellow, green and blue was achieved by inkjet processing of water dispersible polyaniline composite materials and high carbon nanotube loading.[90]

Flexographic printing is based on a soft printing form where raised areas define the printing motif. Ink of low to medium viscosity is metered through a so-called anilox roller with a defined ink volume and transferred onto the printing form cylinder. From the anilox roller it is transferred onto the substrate through slight pressure with the impression cylinder. Although flexo-printing has not yet been shown in the deposition of electrochromic layers it was utilized to manufacture grid based silver networks for ITO-free large area EC devices that also allow fast switching.[61,91]

Large area coating methods for continuous films are *drawbar*, *wire bar*, and *blade coating*. Hereby the wet layer thickness of the film is mainly defined by the gap size of the doctor blade or the characteristics of the bar. Ink is placed in front of the blade/bar and moved along the substrate. These methods allow different wet layer thicknesses and enable homogeneous coating of large areas.[83,85]

Slot-die coating is a pre-metered coating method whereby ink is pumped into the coating head and exits through a thin slot forming a meniscus between the coating lip and substrate. Coating speed, flow rate, and coating width precisely define the wet layer thickness. The method allows homogeneous large area films while patterning is basically limited to stripes depending on the masks inside the coating head. Slot-die coating of ECDs shows considerable potential, but has not yet been widely used. Søndergaard et. al demonstrated that slot-die coating is well suited for deposition of ECPs and large area ECP films were slot-die coated in a R2R process for the fabrication of ITO-free devices.[91] Recently, Jensen et. al showed a novel way of manufacturing ECDs by continuously slot-die coating the constituent layers in one direction.[92]

Spray coating is a coating method where the wet layer film is formed from droplets that are atomized at the spray nozzle. Pressurized gas or air is usually employed for droplet formation, but other principles such as electrospraying and ultrasonication exist as well. An airbrush system is the simplest form of spray coating and often used in the field of electrochromics, which has led to the nickname SprayDOT for the polymers of the PProDOT family.[7] Practical examples of spray coated ECDs include solar-powered EC windows (further described below), while direct photopatterning of spray coated methacrylate-substituted ECP-Magenta has been used to create a patterned EC device.[80] Furthermore, spray coating has been reported to allow easy variation of colorimetric properties due to the fast variation of film thickness and morphologies of different EC polymers.[93]

3.2. Electrochemically Polymerized Devices

By far, the most popular route to fabricate films of conjugated electrochromic polymers onto electrode substrates is by electrochemical polymerization.[9,26,94] However, it is not the optimal choice when considering throughput, reproducibility, material consumption, film quality (over large areas), and ease of film fabrication. As detailed above, processing of soluble polymers offers many advantages over electrochemical polymerization, but the popularity of electrochemical polymerization remains and can be attributed to materials availability and ease of synthesis. Unlike the fields of polymer photovoltaics and polymer light-emitting displays, where there are a large number of commercial sources available to acquire fully conjugated polymers as the active material, this is not the case for electrochromics. Synthesis of conjugated polymers optimized for electrochromic applications still remains in the research laboratory. For those researchers interested in investigating various repeat unit structures in electrochromic devices, it is much more straightforward to synthesize the conjugated monomer to be polymerized via electrochemical methods directly onto the conducting substrate. This highlights one of the main advantages of electrochemical polymerization—the ability to screen a variety of polymer repeat units on small scale. There is the added possibility of not only screening homopolymers via polymerization of a single monomeric species, but also copolymers via polymerization of two or more differing homopolymers at varied feed ratios or polymerization of an oligomeric species to produce a copolymer of controlled structure.[26,95–97]

Typical electrochemical polymerization solutions contain millimolar concentrations of the monomer and 0.1 to 0.5 M electrolyte in the polar solvent of choice. Typical electrolyte salts are lithium-based organic salts (e.g., lithium triflate or lithium bistrifluoromethansulfonimide), tetraalkylammonium salts (e.g., tetrabutylammonium hexafluorophosphate, tetraethylammonium tetrafluoroborate, tetrabutylammonium perchlorate), or ionic liquids (e.g., ethylmethylimidazolium bistrifluorometahnesulfonimide) and commonly used solvents are water or polar aprotic solvents such as acetonitrile or propylene carbonate. Polymerization occurs in a 3-electrode electrochemical cell with working electrodes most often as transparent conductors (such as indium-doped tin oxide, ITO) on glass, or plastic, or reflective electrodes (such as gold on plastic).[47,49,98] Polymerization is initiated via electrochemical oxidation of the monomer in solution, followed by coupling of reactive species and precipitation/deposition onto the electrode surface. Given that the oxidation and subsequent coupling processes are rapid and result in insoluble species, it has been rather difficult to characterize the polymerization process. While the exact mechanism is not known, there are several that have been proposed and covered in detail in the literature.[49,99] What is known is that there are a large number of variables to consider when employing electrochemical polymerization as a film production method as there is a large influence on polymerization parameters and resulting film quality, optical contrast, film thickness, and film morphology.[49,99–101] However, there is no universal correlation between polymerization parameters (solvent, electrolyte, temperature, polymerization method: potentiostatic, square wave, cyclic voltammetry, galvanostatic, etc.)

and resulting film properties. This is because it varies with monomer identity. While there have been intensive studies on the influence of polymerization method on polymer film properties (electrochromic and charge storage applications alike), these have focused on one monomer, or a small subset.

The manufacture of electrochromic devices from electrode-supported polymer films, as mentioned previously, is not a high-throughput endeavor. The most commonly utilized approach is electrochemical polymerization of the working and counter electrode films separately from their respective monomer solutions, followed by assembly of the device in a sandwich-type structure.[17] The difficulties with this route lie in preparation of films on large area substrates as a large volume of monomer solution is required (with much of it going to waste) and the inhomogeneity of the electric field across the electrode substrate.[58] This is especially prevalent with transparent electrodes (such as ITO/glass) as the resistance of the electrode is relatively high (5–20 Ohms/sq) compared to metallic electrodes such as platinum or gold. As will be detailed in following sections, there exist additional methods to prepare devices via electrochemical polymerization that do not require a multi-step process. This can result in elimination of multiple steps during the device preparation process. However, a large fraction of the demonstrations of this concept have been focused on a single polymer film-based device, rather than the dual-polymer devices that have been shown to provide higher contrasts, faster switch speeds, and better durability to multiple switches.[102–104]

4. Device Structure

In general all electrochromic devices employ similar working mechanisms, although the structure of a particular device depends on the utility. ECDs are traditionally divided into absorptive/transmissive (A/T) and absorptive/reflective (A/R) devices based on function and structure. Both types of devices typically have a layered structured as shown in **Figure 3**, but other structures are currently explored in search of improving parameters such as response time, stability or processing, as described in the following sections.

Windows, goggles, spectacles and shutters are typically based on absorptive/transmissive devices as they are designed to switch between an absorptive and a transmissive state. As shown in Figure 3 an absorptive/transmissive device comprises two electrochromic polymers (ECP 1 and 2; primary and secondary) sandwiching an electrolyte layer. The polymers are deposited on transparent electrodes that should allow the viewer to see through the device in the transmissive state. The primary ECP is responsible for the majority of the color change, while the secondary ECP functions as a charge balancing polymer. It should be noted that other compounds have been explored as electroactive counter species in so-called hybrid devices.[105–107] In selecting the counter polymer, several strategies are possible. In dual type devices (a.k.a. the complementary approach) the primary polymer switches complementary to the secondary, which entails that one ECP is cathodically coloring while the other is anodically coloring. (i.e., simultaneous bleaching or coloring of both primary and secondary polymer). This enhances the optical density in the colored state, but lowers the overall optical contrast (ΔT).[108] A further challenge using this approach is the difficulty in finding polymers that are exactly color complementary, which leads to devices where the transmissive state is colored due to the secondary ECP.[17,22,26]

In the symmetrical device approach the primary and secondary polymer is identical. The optical contrast in symmetrical devices is due to the difference of the low transmittance state where one side of the device is fully reduced while the other is fully oxidized (**Figure 4**A) and the high-transmittance state where both ECP films exhibit an intermediate transmittance (the equipotential state, Figure 4B). The symmetrical device structure intrinsically limits the optical contrast as both polymers are never simultaneously bleached or colored. However, this structure facilitates processing and enables construction of devices with semi-interpenetrating networks between the ECP and electrolyte layer, as further described below in "the single layer approach" section.

The minimal color approach employs a secondary polymer that maintains (at best) a colorless state during redox switching. Although the most refined, only a limited number of reports using this approach have been published. The fused poly(thieno[3,4-b]thiophene) reported by Sotzing et al. lends limited absorbance in the visible spectrum in both redox states (sky blue in the oxidized state), as a thin layer was sufficient for efficient charge balance due to the high doping ratio.[109,110] Toppare's group reported on a donor–acceptor polymer comprising a similar fused heterocycle (thieno[3,2-b]-thiophene), likewise showing a high doping level.[111] The N-alkyl substituted polypyrrole developed by Reynolds group differs from

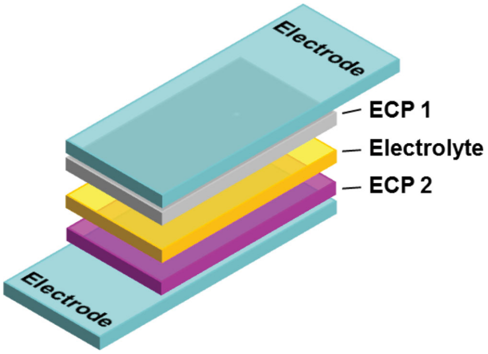

Figure 3. ECD structure for absorptive/transmissive devices. Transparency is required for both electrodes.

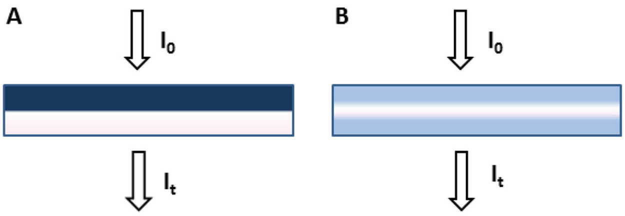

Figure 4. Schematic representation of a symmetrical ECD. A) Low-transmittance state where one layer is fully reduced (top layer) while the other is fully oxidized (bottom layer). B) High-transmittance state where both layer exhibits similar intermediate transmittance. The device is said to be in an equipotential state ($\Delta E = 0$).

the former in being solution processable in addition to being almost colorless.[112]

4.1. Matrix Displays

Displays with individual addressable pixels have been a long standing challenge in ECD technology, and one that is still largely unsolved. The main problem associated with electrochromic matrix displays is crosstalk between the individual pixels, which occurs due to voltage being communicated to pixels peripheral to the one intended for switching.[113,114] In order to address this challenge the group of Berggren proposed a method that utilizes electronic paper, a term constituting cellulose-based paper coated with polyethylene and further functionalized by deposition of ECPs and organic transistors.[115] One advantage of this approach is the use of high throughput printing techniques as described in the section on coating techniques.

The "smart pixel" design (shown in **Figure 5**) exploits the electrochromic and conductive properties of PEDOT:PSS. The conductive properties are electrochemically tunable, whereby PEDOT:PSS functions as a transistor, allowing the display voltage to be reduced by a factor of 5000. Both the gate and display are operated between 0 V and +2 V, and the switch between the various redox states of PEDOT is reversible assuming that overoxidation does not occur. The response time of these smart pixels was reported to be 5 seconds for a 13 × 30 mm^2 (95% switch), and using an electrolyte that comprised a white opaque filler, the counter electrode was hidden (intrinsically prohibiting any transparency in the device). In further developing the smart pixel, a vertical structure was designed that increased the fill factor of the display (i.e., the ratio of switchable area versus total display area).[83] In addition to an increase in fill factor, the vertical structure reduced the response time due to shorter ionic drift. A disadvantage of this was that since the top electrode (the one seen) became larger than the counter electrode, a blooming effect as a consequence of lateral charge transport was observed.[91] In a recent report on smart pixel design, the transistor is an integrated part of the ECD in which the drain electrode in the transistor functions as the counter electrode in the ECD.[85] While the prototypes from this new design show increased response times and limited optical contrast, the general design, manufacture, and mode of operation show promise for addressable pixelated ECDs. The group has also reported on a flexible passive matrix addressed electrochromic display, that employs carbon paste as the hidden counter electrode.[116] This structure should simplify manufacturing, and through this inert counter electrode, water is believed to complement the redox reactions of the primary polymer.

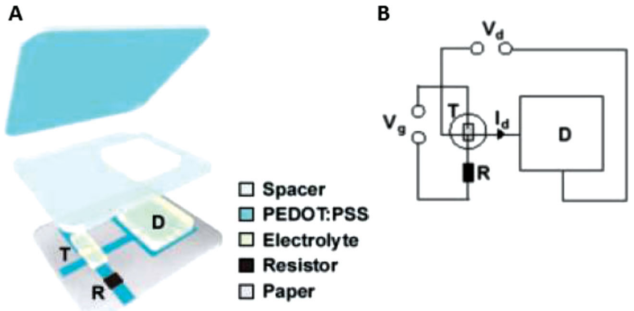

Figure 5. A) Smart pixel structure consisting of a display cell (D) a resistor (R) and a transistor (T). The turquois color corresponds to PEDOT:PSS coatings and the cyan colored patches to electrolyte gel. B) Electrical diagram representation of the smart pixel. The display cell voltage (V_d) and gate voltage (V_g) are supplied from two different power sources. The gate voltage controls the updating current I_d. Reproduced with permission.[115] Copyright 2014, John Wiley & Sons Ltd.

4.2. "All-Plastic" and ITO Free Devices

To address the problems associated with a liquid or semi-solid electrolyte the group of De Paoli reported on all-plastic ECDs comprising blends of ECPs and elastomeric poly(epichlorohydrin-co-ethylene oxide) or poly(acrolynitrile) as the electrochromic layer.[117–119] Not entirely "all-plastic" (the substrates contained indium doped tin oxide), this strategy aimed at synergistically combining the properties of the two blend components. The optical contrast and response time in the blends were found to improve relative to the "pure" ECPs and, as the optical charge capacity of the two were identical, this was attributed to morphology changes in the ECP due to blending with the elastomer. In addition, it was found that the lifetimes of the devices employing blends were increased as well. The solid state electrolyte used in the majority of these devices consisted of poly(epichlorohydrin-co-ethylene oxide) (trade names HydrinC or Epichlormer-16) and $LiClO_4$. The redox states of the electroactive polymers were preset before device assembly either electrochemically or chemically through doping,[118–120] in order to enhance the optical contrast and device lifetime. De Paoli et al. also showed an impressive 75% optical contrast for a 20 cm^2 solid state ECD, but unfortunately the optical contrast decreased to 42% after 100 double potential steps (dps) at +0.9 V/–0.8 V; 20 second pulses, which was attributed to uncompensated charge balance between the electrodes.[121]

Mecerreyes et al. reported on a very simple device construction using PEDOT:PSS simultaneously as an electrode and an electrochromic layer.[63] Commercially available PEDOT coated foils were employed in this flexible all-polymeric device, and despite limited optical contrast (15%) due to the symmetrical structure, the flexibility and substitution of ITO is appealing. The operational stability of these devices was markedly increased by using polymeric electrolytes composed of ionic liquids (ILs) and polyionic liquids, in agreement with other reports on ILs as charge carriers in ECDs.[122–124] This contribution followed a report by the Reynolds group, where ITO likewise was substituted by PEDOT:PSS as the transparent electrode material.[23] This "first truly all-polymeric electrochromic device" employed PProDOT(Me_2) and PBEDOT-*N*-MeCz as the cathodically and anodically coloring polymers (respectively), and showed an optical contrast of 51%. A recent publication presents symmetrical devices with increased optical contrast of 22% for devices comprising a poly ionic liquid electrolyte and PEDOT as the electrochromic layers sandwiched between ITO coated electrodes.[125]

In order to substitute ITO as electrode material, Jensen et al. reported on ECDs having thin silver grids on flexible substrates as the electrodes.[62] In addition to alleviating the need for ITO, this development also had the significant implication that the electrodes could be printed in a full additive manner directly onto protective barrier foil which increased the device stability.

4.3. Single Layer Approach

To simplify device structure, a strategy combining the electrochromic polymer with the electrolyte in one sole layer has been pursued. This single layer approach aims at optimizing the manufacturing process by reducing the number of deposition steps, avoid electrolyte leakage, reduce materials waste and overall increase the stability of the device. In a report from DuPont, a carbazole chromophore was grafted onto poly(epichlorohydrin-co-ethylene-oxide) chains, forming just one electrochromic layer.[126] In another report, the electrochromic species (a viologen) was simply heated in thermoplastic poly(vinyl formal) (PVF) matrix and pressed into a self-supported film.[127] The simplicity in the approach is very attractive and the thermoplastic polymer PVF shows strong adhesive properties that increase the mechanical stability of the device. Other strategies for the single layer approach rely on in situ polymerization of the ECP inside the electrolyte matrix, forming a semi-interpenetrating polymer network (semi-IPN). This is elegantly exemplified by reports from the Chevrot group where EDOT or 3,4-(2,2-dimethyl propylenedioxy)thiophene (ProDOT-Me$_2$) was oxidatively polymerized in situ inside a crosslinked poly(ethylene glycol dimethacrylate)/poly(ethylene glycol methacrylate) matrix.[104,128] By controlling polymerization time and solvent composition, free standing electrochromic films where fabricated with the ECPs confined to the outer regions of the films, thereby leaving the interior matrix ECP free and preventing the device from short circuiting. The optical contrast (above 30%) of these devices showed an increase compared to other symmetrical devices, and the response times ranged from 30 to 60 seconds depending on the direction of the switch.[63]

A similar strategy that relied on electrochemically polymerizing a monomer or polymer precursor inside a solid state device was reported by Sotzing's group.[102,103] This in situ approach (shown in **Figure 6**) eliminates the need for rigorously cleaned substrates for electrochemical deposition of polymers and electrolyte baths thereby minimizing solvent usage. Several polymer and solvent systems were investigated with lithium salts in a PEG/PC solid state matrix yielding the highest photopic contrast.[129] The response times for devices (4–12 cm^2) were in the order of 1 to 4 s (90–95% of a full switch) depending on the direction of the switch. One of the challenges using electropolymerization is unevenness in the polymer layer when up-scaling to larger substrates, but in using this approach large defect free devices of 105 and 171 cm^2 were realized, with the latter showing a photopic contrast of 48%.[129,130] In a recent development, acrylate substituted-ECPs were crosslinked with the electrolyte matrix thereby significantly increasing the electrochemical stability of the resulting devices.[131]

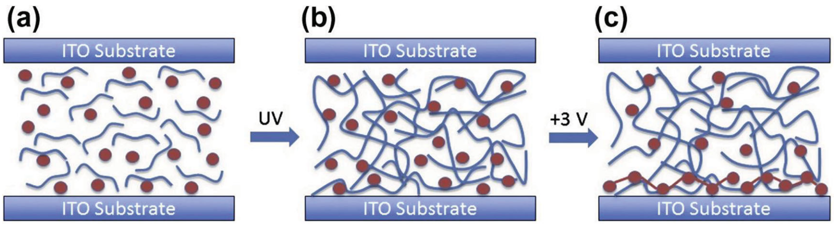

Figure 6. Schematic diagram for in situ polymerization. A) Solution containing liquid monomer electrolyte and EC monomers sandwiched between two ITO coated substrates, B) Photo-crosslinking of the liquid electrolyte yielding a solid electrolyte. C) Electrochemical polymerization of EC monomers at +3 V, creating a semi-IPN. Reprinted with permission.[129] Copyright 2014, Elsevier.

4.4. Reflective ECDs

While much of the focus in the literature has been towards absorptive/transmissive, window-type, ECDs, it may be the absorptive/reflective, display-type, ECDs that hold promise for commercial applications. Applications that would utilize window-type devices include, obviously, building, automobile, and aircraft windows, but also eyewear (e.g., pilot visors, military and skiwear goggles, and sunglasses). Many of the requirements for such applications are relatively stringent and are difficult for even the best electrochromes (solution-phase organics/inorganics, metal oxides, etc.) to find applications. These requirements include a highly absorptive dark state, a transmissive state of at least 80% (higher in many cases), and color neutrality in both states (nearly black when colored and colorless when bleached). Other requirements may include low switching voltages, a bleached fail state, a minimized "irising" effect when switching, and others. While a color neutral, nearly black absorptive state is required for absorptive/transmissive devices, colorful, vibrant states are desired for many reflective display applications. These applications include point-of-purchase advertising, e-paper, e-books, textiles, decorative applications, and billboards.[55,82,132,133] These applications can take advantage of the mechanical flexibility and color vibrancy found in electrochromic polymers. Other applications that may not require color vibrancy, but large near infrared contrasts include adaptive camouflage, thermal control panels (terrestrial and space-related), and fiber optic telecommunications.[134–136] Given that ECPs exhibit near infrared contrasts that reach 70–90%, these materials are ideally suited.

Of the reflective electrochromic devices reported in the literature, a large majority that relies on visible region electrochromism are diffuse-reflective. These include the aforementioned paper-like electrochromics of Berggren et al., which most commonly utilize PEDOT:PSS printed onto paper substrates with a variety of patterning and electrolyte printing methods explored.[82] The devices in these demonstrations typically utilize a lateral configuration whereby the working and counter electrodes are printed onto the same substrate which can limit switching speeds and contrasts, but do offer

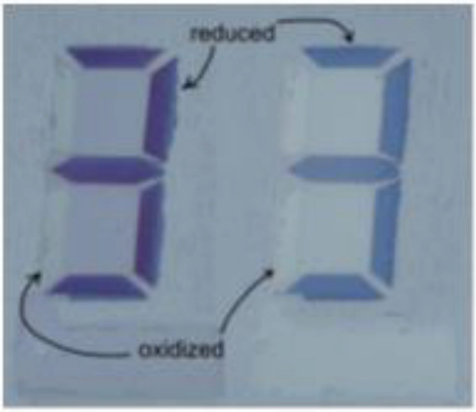

Figure 7. Enhancement of the electrochromic contrast of a seven-segment paper-like display by deposition of a ProDOT-based polymer on top of PEDOT:PSS (left device) compared to use of PEDOT:PSS alone (right device). Reprinted with permission.[82] Copyright 2009, Royal Society of Chemistry.

a highly simplified fabrication method. An example of one of these devices that utilizes a bilayer structure of a ProDOT-based polymer printed on top of PEDOT:PSS to achieve a high contrast device is shown in **Figure 7**.

In addition to paper-like devices, there is increasing interest in textile-based devices. Electrochromic polymers offer an advantage in this application over other electrochromes given their inherent mechanical flexibility and deposition on a variety of flexible and polymeric substrates.[55,132,133] Approaches include impregnating textile fibers with an electroactive polymer (e.g., PEDOT:PSS) that renders the fabric conductive, or incorporation of conductive fibers or wires to establish the electrode. The fabric is coated with electrochromic polymer or monomer followed by either chemical or electrochemical polymerization. The ultimate goal would be to have devices that do not require protective layers, but many examples do as the non-optimized electrolyte requires containment.

Those reflective devices that capitalize on the large NIR contrasts of ECPs utilize metallic reflective underlying electrodes or the semi-interpenetrating network previously described.[134] The semi-interpenetrating network devices are comprised of an ECP (e.g., PEDOT) polymerized on either side of a network polymer such as nitrile butadiene rubber and/or poly(ethylene oxide) in the presence of electrolyte. In this device, the reflectivity is measured from one surface that is switching between absorptive and bleached (in the NIR) states relative to the same polymer switching on the other side. However, the polymer on the opposite side does not contribute to the optical switching of the device, only acting as a charge-balancing layer. This allows the large NIR contrast of the front-facing polymer to be measured without contrast limitations of the counter polymer.

Another NIR reflective ECD approach utilizes an outward-facing gold electrode onto which the electrochromic polymer is deposited. Early examples utilized a metallized plastic substrate with parallel slits cut into it and the counter electrode placed behind. The slits allowed ionic contact between the front and back electrodes. Later examples have utilized a metallized porous membrane with improved contrast and switch speed. Such a device configuration is shown in **Figure 8**. The use of gold as the reflective substrate electrode is advantageous as gold has a high NIR reflectance. These device types have been proposed as variable emittance skins for aircraft/spacecraft thermal control, NIR camouflage, and fiber optic variable optical attenuators.

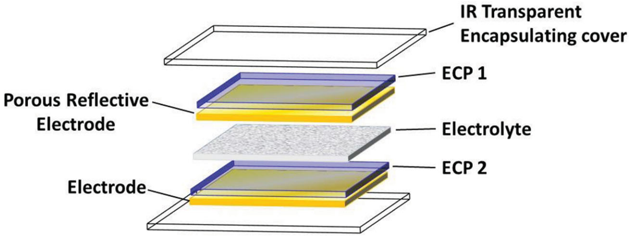

Figure 8. Device layout schematic for a NIR reflective ECD.

5. Integrated Electronics

An obvious advantage of electrochromic devices comprised of thin polymer films is the possibility for manufacturing devices wherein the ECD is integrated with other organic thin film technologies such as organic photovoltaics (OPVs), dye sensitized solar cells (DSSCs), organic field effect transistors (OFETs), organic light emitting diodes (OLEDS) or electrochemical super capacitors (ESCs).[75,83,85,137–141] By integrating ECDs with e.g., OPVs, two significant objectives are realized: 1) A self-powering lightweight ECD that expands the usability of ECDs in consumer electronics as these become independent of a grid connection. 2) Analogous equipment requirements for processing. Since the two components share common traits concerning, for example, solubility and viscosity, the option of using similar coating techniques would simplify the overall fabrication process of these integrated devices; a further step towards commercialization. Matching of the low power requirements and bistability of a solution processed ECD, with an OPV was explored by Jensen et al. in printed module devices wherein one OPV powered the oxidation of the ECD while a second OPV powered the reductive process (**Figure 9**A).[75] These modules showed an optical contrast of 44% (vs ref) and response times of 4–5 s for a 95% shift. As the modules were examples of solar powered ECDs the photochemical stability of the ECPs was evaluated. Full sun illumination (AM1.5G, 1000 W/m^2, 45 °C) for 100 h led to a decrease in absorbance of 20% and a loss in ΔT of 25%. The relative limited degradation was a result of the plastic foils used for encapsulation of the ECD/OPV modules, as these were later reported to be effective in shielding the active polymer layers from photodegradation.[62] The report also showed that a solid state electrolyte is important both for ease of processing and to prevent electrolyte leakage.

Recent work from Dyer et al. describes a vertically integrated OPV/EC device wherein the two components share a common PEDOT:PSS transparent electrode as depicted in Figure 9B.[137] PEDOT:PSS was employed to function simultaneously as electrode material in the ECD and as hole blocking layer in the OPV cell. This report highlights the difficulties in vertical

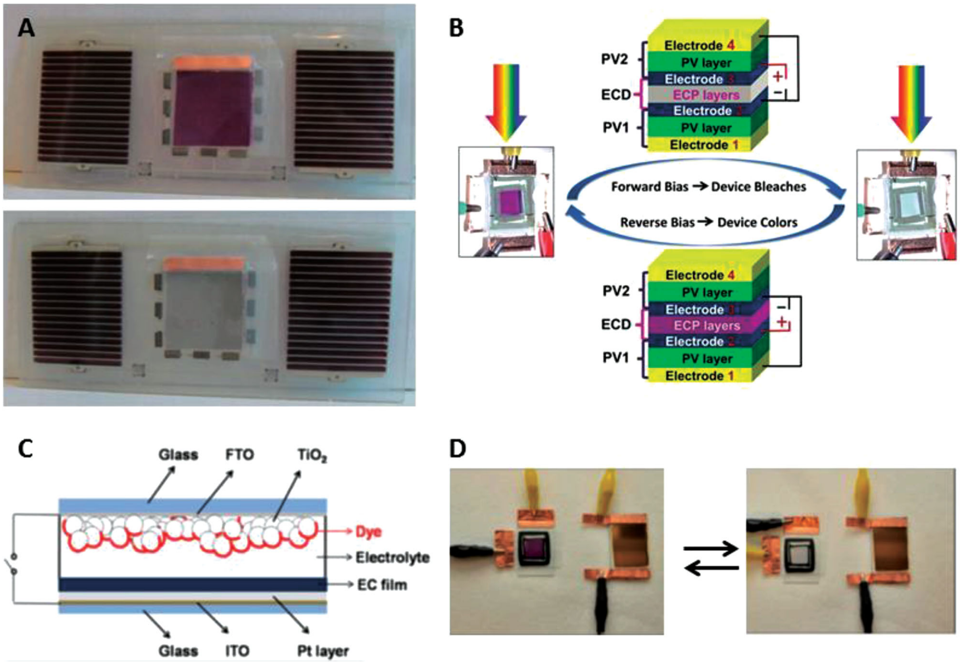

Figure 9. Integrated electronics. A) An ECD powered by an OPV. Reproduced with permission.[75] Copyright 2011, John Wiley & Sons Ltd. B) A vertically integrated ECD/OPV module. The two components share the same PEDOT electrode. Reproduced with permission.[137] Copyright 2014, John Wiley & Sons Ltd. C) Structure of a photoelectrochromic device. Reprinted with permission.[139] Copyright 2011, Elsevier. D) An ECD powered by an electrochemical supercapacitor. Reprinted with permission.[140] Copyright 2013, American Chemical Society.

integration of the two components as the efficiency of the OPV cell was found to decline following ECP deposition; a deleterious side effect that was attributed to the organic solvents used for spray coating. Interestingly, the authors investigated the functionality of the devices when taken from optimized laboratory conditions (i.e., artificial sun; 100 mW/cm^2) and into less ideal conditions (e.g., reduced solar intensity as an example of cloudy weather). As an example of this the devices showed an increased response time from 3 to 6 seconds when the intensity was reduced to 25 mW/cm^2, but an optical contrast ($\Delta T = 20\%$) similar to that gained from 1 full sun illumination.

Dye sensitized solar cells have also been used as the power source in self-powered ECDs (named photoelectrochromic devices, PECDs, by some authors) as illustrated in (Figure 9C). Hsu et al. electrodeposited poly(3,4-(2,2′-diethylpropylene-dioxy)thiophene (PProDOT-Et$_2$) onto the counter electrode in a DSSC and investigated the effect of several redox electrolytes.[138,141]

The I^-/I^{3-} redox couple resulted in the fastest response times (app. 3 seconds) but gave a rather limited optical contrast of 14%. On the contrary PECDs comprising the Br-/Br^{3-} redox couple showed an optical contrast of approximately 26%, but extended response times of several minutes, although these were reduced by increasing the bromide concentration. Xu's group reported on a 4 cm^2 PECD showing increased optical contrast (38%) and response times of 1–4 s using poly(3,4-(2,2′-dimethylpropylene-dioxy)thiophene (PProDOT-Me$_2$), a ruthenium dye and a Pt catalyst.[139] Progress in PECDs shows potential as a feasible way of integrating ECDs, however using liquid electrolytes might hinder effective mass production and large devices due to leakage and hydrostatic pressure.[142] Besides integrating light harvesting devices with ECDs, electrochemical supercapacitors (ESCs) have recently been demonstrated as a power source for ECDs.[140] PEDOT polymerized at several charge densities was employed as an ESC and used to switch a 1.6 cm^2 ECD. Employing ESCs take advantage of the low voltage used for switching ECDs and the memory effect exhibited by most ECPs, thereby preventing the need for constant power e.g., from a battery. The electrochemical stability of the ESC also paired well with that of an ECD by retaining 80% capacitance following 400 000 cycles between 0 and 1 V.

6. Device Analysis and Optimization

6.1. Analysis

The techniques used for analysis and characterization of electrochromic polymers are in general valid for devices as well, but some important differences concerning electrochemical analysis need attention. The major difference is that ECP films are usually electrochemically characterized in a three electrode setup where the potential is applied relative to a known reference potential while an overwhelming majority of devices lack a reference electrode. Therefore, the device is considered a two-electrode cell where the potentials reported are those of a potential difference between the working and counter electrodes—not an electrochemical redox potential as it is in a 3-electrode cell. This is shown schematically in **Figure 10** where the color gradient of a cathodically coloring and an anodically coloring polymer, over their electrochemical switching voltage windows (versus a standard reference, Ag/Ag$^+$) are shown. When combined in a dual polymer device, the cell voltage for

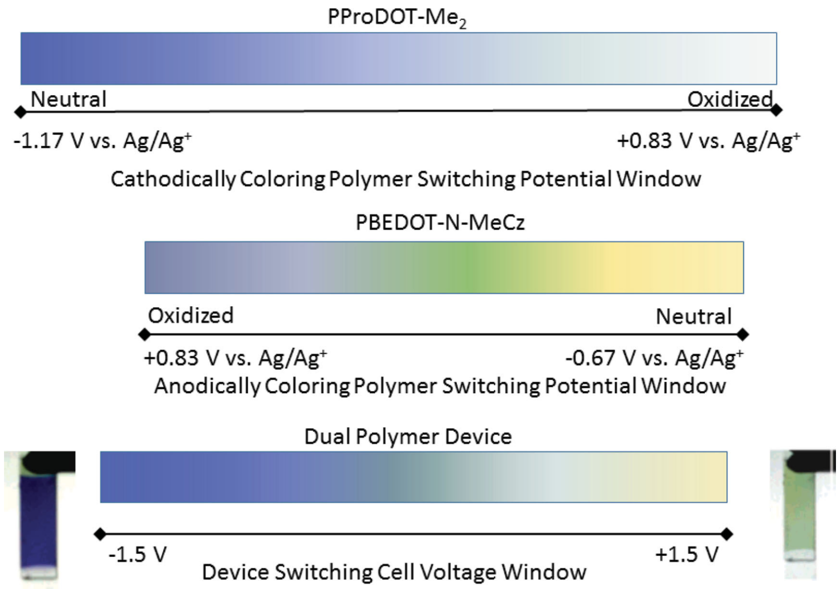

Figure 10. Illustration of the combination of two complementary electrochromic polymers towards a dual polymer ECD. The cathodically coloring polymer is ProDOT-Me$_2$ which is neutral at –1.17 V vs Ag/Ag+ and fully oxidized at +0.83 V vs Ag/Ag$^+$. The anodically coloring polymer is PBEDOT-N-MeCz that is fully neutral at –0.67V vs Ag/Ag+ and oxidized at +0.83 V vs Ag/Ag$^+$. When combined in a dual polymer device, the cell voltage (potential difference across the device) required to achieve full contrast is –1.5 V to +1.5 V. Voltages and color data are taken from the literature.[20] Photographs adapted with permission.[156] Copyright 2002, American Chemical Society.

the device is –1.5 V to +1.5 V—the potential difference across the device. As these two polymers switch within the same voltage window (PProDOT-Me$_2$ having a slightly wider voltage window than PBEDOT-N-MeCz) the full color contrast of both is attained at the operating cell voltage for the device.

The absence of a reference electrode impedes control of the electrode potentials and consequently the redox states of the polymers. In the cases of two polymers with non-overlapping voltage windows or narrow voltage windows for stable switching, this lack of control of the electrode potential can be detrimental. For prolonged lifetime, ECDs should be composed of polymer films that are redox complementary, that is, the oxidation potential ($E_{\text{p,ox}}$) of polymer 1 should correspond to the numeric value of the reduction potential of polymer 2 ($E_{\text{p, red}}$).

Naturally, knowledge and control of the redox states are important in order to optimize device performance and stability and in a report on electrochemical characterization in device-like settings the setup shown in **Figure 11** was used to measure the redox states at the two electrodes.[143] Following determination of the electrochromic potential windows, the setup was used to determine charge consumption of the constituent polymers and how the redox charge ratio between the counter and working electrode affect this. This work targeted the main challenge in device analysis—namely "getting inside" an assembled device in order to obtain reliable information about the redox chemistry at the constituent electrodes. Addressing this, Xu et al. reported on an EC window in which a reference silver foil was incorporated to imitate a three electrode cell.[144] The resulting devices showed increased stability (presumably by control of the WE potential) and switched at lower potentials compared to an equivalent two-electrode device.

6.2. Optimization

Optimizing the performance of electrochromics can be done on the materials as well as on the device level. Optimization on the materials level is exemplified by Reynolds et al., that through alkyl and alkoxy substitution of polypropylenedioxythiophenes, poly(ProDOTs), the optical contrast increased and lowered the response times.[19,24,25,145,146] On the device level the optical contrast is dependent upon the thickness of an ECP film, and therefore it is advantageous to know the optimum film thickness for this value. Lim et. al presented a systematic prediction of the optical contrast of an electrochromic material in a device, based on a coating parameter reflecting the deposition of ECP (e.g., concentration of solution, coating speed, number of cycles etc.) and hence thickness of the EC film (assuming linearity between the two).[147] Optimizing the optical contrast has been further explored by other groups, and it was found that dual system ECDs (the vast majority of ECDs) limits the maximum contrast compared to a single ECP film.[108,148] Kawahara et al. studied the effect of varying ratio of the primary and counter electrode thickness, and observed a 12% increase in color contrast (ΔE^*) by employing a counter electrode four times thicker than the primary electrode.[60] Likewise Seshadri et al. found the polymerization charge densities (i.e., thickness) leading to the highest photopic contrast in PEDOT and poly (3–6-bis-(2-(3m4-ethylendioxy)thienyl)-*N*-methylcarbazole (PBEDOT-NMCz) dual polymer devices to be ca. 10 mC/cm^2 and 2 mC/cm^2, respectively.[58] Though, optimizing the thickness ratio between the primary and counter ECP increases the optical contrast of the resulting devices, it is not necessarily the optimal thickness electrochemically. The ratio of redox charge density (i.e., the electrochromic charge) of the two ECP films should also be as close to unity as possible in order to increase

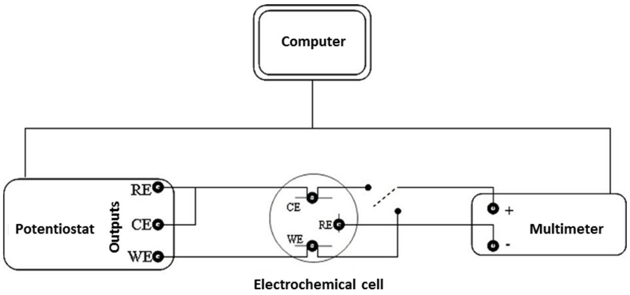

Figure 11. Schematic of instrumental setup used to measure potential and redox states at individual electrodes. Reproduced with permission.[143] Copyright 2007, Elsevier.

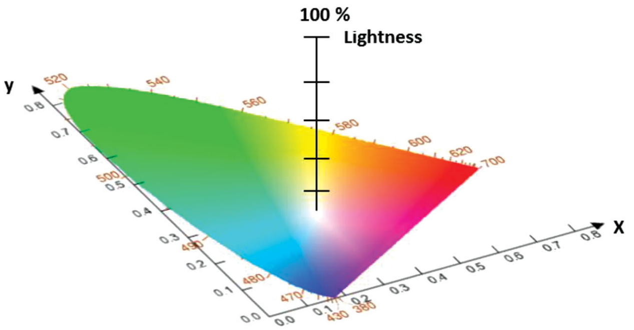

Figure 12. CIE 1931 *xy*-chromaticity diagram. The *x* and *y* values are calculated from the tristimulus values. The numbers lining the horseshoe shaped diagram corresponds to approximate wavelengths. Protruding up from the diagram is the lightness of the color. Any color is represented by a point the diagram.

the electrochemical stability, and this might compromise the optimal optical thickness.[112,143,149]

Color optimization has traditionally been developed through chemical modification of the constituent polymers (see references in the introduction), but research on color control through device engineering has recently begun. Color analyses are done using spectroelectrochemical or colorimetric techniques, where the former measures the absorbance/transmittance at a given potential in a spectrophotometer, while the latter uses a colorimeter to quantify the color of the ECP/ECD in a given color system. Several color systems exit, with the The Commision Internationale de l'Eclairage (CIE) as the one commonly used in ECP/ECD description.[20,150] The CIE system is based on color matching functions that are converted to tristimulus values. These reflect the human perception of color, and can be represented in various 2- or 3-dimensional color spaces or in a *xy*-chromaticity diagram as exemplified in **Figure 12** (For a full description of the CIE color system, the reader is directed to the cited references).

In ECDs the color from the constituent polymers can be calculated from the absorbance spectra. In the *xy*-chromaticity diagram in Figure 12 the color of the resulting ECD can be predicted to lie on the line connecting the points of the two polymers as a lightness-weighted average.[20] In effect a dual polymer ECD can be thought of as a lamination of two polymers which was described by Brotherston et al. along with other ways of tuning the colorimetric properties of ECDs.[84] In another interesting study on applied color mixing Shin et al. reported on ECDs absorbing in the entire visible range, as a result of depositing several ECPs onto the ITO/glass electrodes as shown in **Figure 13**A.[151] This report showed that order and type of deposition technique of the individual layers influences the electrochromic performance of the devices due to factors such as interfacial adhesion and resistance. Showcasing this, it was found most favorable to deposit PEDOT (by vapor phase polymerization) onto poly(3-hexylthiophene) (P3HT), as the PEDOT surface roughness limited the interfacial contact if the deposition was done the other way around. The multilayered nature of these devices subjects them to "the lowest common denominator" in regards to potential requirements and response times. This means that to fully switch one polymer the potential requirements of the other polymers are exceeded, which may cause unwanted side effects and degradation.[76,152,153] The practical challenges for subtractive color mixing in ECDs were also addressed by Bulloch et al., in a study comparing inventive, yet simple dual-active (a.k.a. pseudo three-electrode, see Figure 13B) ECDs to a stacked device architecture (simply stacking 2 or more ECDs).[154] Due to the difference in optical interfaces, the colors of the dual active structure were found to be more saturated and the transmissive states more bleached than the stacked devices. The dual active structure allows for fine tuning of color, but a third electrode needs to be added to complete the cyan-magenta-yellow primary system and the lightness of the devices was likewise uncontrollable.

7. Perspectives in the Field

The three most important areas where improvements would significantly impact the applicability of ECDs and push them further towards application are the electrode, the electrolyte and the fabrication methods. Since the electrochromic device in terms of light is a passive device, reflection losses are critical to the perception of the device and from this point of view it is unlikely that electrochromics will ever find applicability where high optical transmission is required. Application should be sought where there is a desire to attenuate light to a varying degree such as shades or blinds or for billboards where the inherent optical absorption in an electrochromic device can be counteracted by an excess of backlight. This however still underlines the necessity to develop highly transmissive electrode systems based on printed/imprinted grids or nanostructures such as nanowires. Another aspect of the electrochromic device is that the switching between color states requires movement of ions and therefore some sort of electrolyte material that presents the possibility for ionic mobility. A solid state electrolyte based device which is required in manufacture thus imposes the requirement of a printable electrolyte system that can be dried and remain dry to the touch and enables

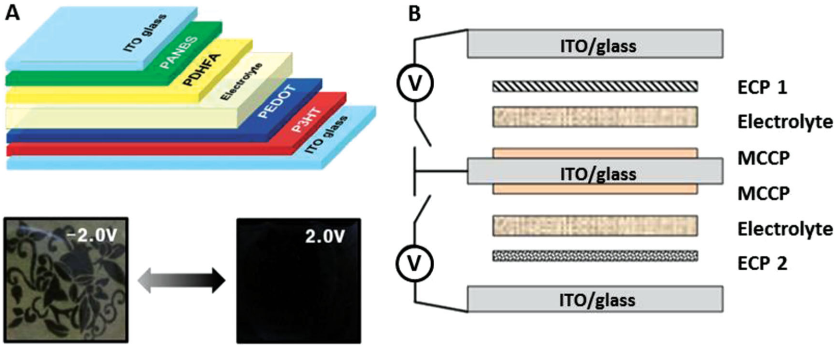

Figure 13. Multilayered electrochromic devices. A) Top: Structure of the multi ECP device presented in a previous study.[151] Bottom: an example of the device switching between −2V and +2V. B) Structure of a dual active device. The two ECDs share the ITO/glass electrode in the middle, which coated on both sides with MCCP presented in another study.[154]

good adhesion at the interfaces. The electrochromic device is a multilayer structure that typically has the electrolyte in the middle and therefore the electrolyte shares two interfaces with the active materials in the device. Those interfaces must be strong if robust operation is to be expected and this is especially critical for flexible devices. Here it is likely that chemical crosslinking or post-application curing methods will need to be developed. Finally the electrodes, electrolytes, active materials and curing methods must be developed for the desired processing methods that most likely will be a roll-to-roll method using flexible substrates. The materials must thus be developed for the process and the development phase where materials, process, and device evolved together will extend over some time before maturity can be expected. The recent progress on creating materials that are electrochemically stable and robust in operation as a device however confirms that the electrochromics are very likely to find a significant share in our sustainable future.

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