Flexible Electrochromic Elements for Adaptive Camouflage

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ABSTRACT

Optical camouflage alone is no longer sufficient, due to the development of sensor-based signal and signature recognition, which can detect different wavelengths of the electromagnetic spectrum (visible [VIS, 380 – 780 nm], near-infrared [NIR, 780 – 2500 nm], thermal infrared [TIR, 8 – 12.5 µm] or radar [2.4 – 3.75 cm]). A modern, high-performance camouflage element should provide protection over the widest possible range of the electromagnetic spectrum and would therefore be called a multispectral camouflage system. This tunability in the VIS and NIR is possible with electrochromic (EC) materials. By applying an electric voltage or current, a colour change of the EC materials is induced, which actively controls the absorption, transmission, and reflection of surfaces and creates an adjustable camouflage pattern.

1.0 INTRODUCTION

Camouflage is crucial for military operations, as it allows military personnel and equipment to blend in with their surroundings and avoid detection by the enemy. It can effectively help to protect troops from enemy fire, make it easier to launch surprise attacks, and allow for covert operations to be carried out without detection. Camouflage techniques have evolved significantly over time, with modern military forces utilizing advanced materials and technologies to create highly effective camouflage patterns. Military camouflage technologies are being developed toward lighter, more comfortable and intelligent elements as effective countermeasures for artificial intelligence (AI). To date, there are only non-adaptive solutions for camouflage applications, which are limited to their terrain-specific environments (e.g., mixed-coloured garments and tarpaulin). Ideally, adaptive camouflage could exhibit changes to the object's surroundings by actively and independently varying its patterns and colours, acting as perfect concealment from Visible (VIS) and Near-Infrared (NIR) detections. Flexible electrochromic (EC) elements have significant military relevance due to their ability to adapt and enhance operational capabilities in various scenarios. These elements can provide situational awareness and tactical advantage to military personnel in the field. EC materials can be incorporated into military vehicles, uniforms, and equipment to allow for rapid adaptation to different environments. By adjusting the colour or pattern of the material, it becomes possible to blend in with the surroundings or mimic different objects, enhancing stealth and reducing the chances of detection. Furthermore, the flexibility of these elements makes them lightweight, durable, and adaptable to different environments, making them ideal for military operations in challenging terrains. Overall, the military application of flexible EC elements can greatly enhance the effectiveness and efficiency of military personnel.

1.1 Basics of Electrochromism

The wide range of colour-changing materials used in commercial products can be classified into two major groups–active or passive materials, depending on how the change of the colour is activated. The passive colour-changing materials, such as photochromic [1] or thermochromic [2] materials react to the changes in environmental parameters, such as light and temperature, respectively, while active materials, can be switched on and off on demand. One group of active materials is known as electrochromics, which change colour in response to an electrical stimulus [3]. The obtained redox states exhibit different optical properties, although high transparency is maintained in both states. If the absorption band is in the VIS range, the EC layer shows a characteristic colour. High transmittance over the whole VIS range is achieved (e.g., by shifting the absorption band into the NIR range or by suppressing electronic transitions). Inorganic and organic EC materials are typically deposited as thin films onto a variety of substrates, such as glass or plastic, making them highly versatile and compatible with a wide range of applications.

The general architecture of a battery-like EC element is shown in Figure 1. It consists of two electrodes and an ion-conducting and electrically insulating electrolyte in between. The first electrode comprises the transparent conductive substrate and the EC layer. The second electrode consists of the transparent conductive substrate and the ion storage or complementary switching EC layer. By applying an electrical voltage or current to EC materials or elements, a change in the optical properties (absorption/transmission and reflection) results from the change in the redox states. An advantage of EC materials and elements is their fast response and low power consumption (i.e., low operating voltages [< ±2 V]). This means that they can be switched on and off quickly and efficiently, reducing the risk of detection and conserving battery life.

EC technologies are widely known in the civilian sector for architecture, automotive, and aircraft [3], [5]. Some of the EC materials (inorganic and viologen based) have already been commercialised and can be found in high-end automotive dimming interior rear-view mirrors (Gentex corporation), the Boeing 787 Dreamliner windows, and in buildings (e.g., SageGlass, View, and ChromoGenics).

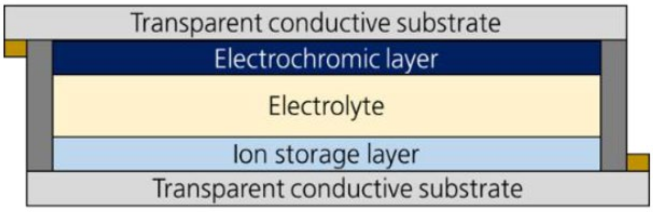

Figure 1: Architecture of an EC element.

1.2 Electrochromic Materials and Elements for Adaptive Camouflage

EC materials and elements have been investigated for camouflage applications, as they can be used to create a dynamic colour-changing surface that can adapt to different lighting conditions and backgrounds. For example, researchers have developed EC polymers, metal oxides, and metal complexes that can change colour in response to an electric field. [6], [7], [8], [9], [10] An interesting class of EC materials are EC polymers, such as polyphenylene, polyaniline, polypyrrole, polycarbazole, polythiophene, and their derivatives [3]. The characteristic EC properties of conjugated polymers result from an extended conjugated π-electron system, creating a band-like electronic structure. In general, electrochromism in conjugated polymers occurs through changes in the p-electronic character of the polymer, accompanied by reversible insertion/extraction of counterions in the electrolyte upon electrochemical oxidation and reduction [6]. Leclerc [7] et al. reported three new poly(2,7-carbazole) derivatives, which exhibit green colour in their neutral state and a brownish hue when oxidized.

The fabricated EC elements are showcased to be used for military camouflage. Meng [8] et al. demonstrated chameleon-like fabrics based on donor-acceptor conjugated polymers, with the 3,4-ethylene dioxythiophene (EDOT) as the donor and the modified quinoxaline as the acceptor, which reversibly changes between grass green and sand yellow. Another interesting study by Zenkina et al. focuses on new EC materials by fine modulation of the colour of the surface-confined metalorganic monolayer [9]. The EC elements can switch between different shades of green, initially, to a yellowish hue after a voltage is applied. The accessible colours fulfil the requirements for chameleon-like camouflage materials and can mimic conditions of various natural environments including forests and sands. Recently, Bera et al. reported the synthesis of a dual redoxresponsive heterobimetallic (osmium and ruthenium) supramolecular polymer as a multicolour EC material that can also be used for camouflage applications [10]. Multi-coloured polymers with high colouration efficiency, vivid colours, and fast response could open new possibilities for the military use of electrochromics (e.g., soldier protection or camouflaged vehicles). There is ongoing research on this topic, but to date, there are no known applications exceeding the laboratory or prototype level. In addition, many developments are confidential, which makes it difficult to assess the current state-of-the-art of applications.

While these studies show promise for the use of EC materials in camouflage, further research is needed to address challenges such as durability, switching performance, colour variability, power consumption, and cost-effectiveness. Nonetheless, the potential for dynamic, adaptive camouflage using EC materials is an exciting area of research that could be interesting for military applications and beyond.

However, it is important to note that EC materials and elements can be sensitive to environmental factors, such as sunlight, humidity, and temperature, which reduces their effectiveness. To address this issue, strategies have been explored to improve the stability of EC materials [11], [12], [13]:

- **Modification of the materials:** The stability of EC materials can be improved by modifying their chemical structure. This can be done by adding functional groups to the materials or altering the chemical composition to improve stability.
- **Encapsulation:** The use of encapsulation techniques can protect EC materials and elements from environmental factors that may degrade them. For example, encapsulating the materials in a polymer matrix or using a protective coating can help to maintain their stability.
- **Use of additives:** Additives can be added to EC materials to improve their stability. For example, the addition of antioxidants or stabilizers can help to prevent the degradation of the materials over time.

2.0 FLEXIBLE ELECTROCHROMIC ELEMENTS

In this study, the chosen EC polymer for controllable camouflage surfaces for use in mobile multispectral camouflage systems exhibits a property profile with several advantageous features (e.g., a colour-neutral and highly transmissive bright state and high optical contrast). This polymer can be deposited as a thin layer on flexible substrates (PET-ITO or other transparent conducting films) using a roll-to-roll slot-die coating by a proprietary process. The film thickness can be adjusted by the web speed and the dosing volume of the coating solution. After coating and drying, the thin film electrodes have to be rinsed and pre-conditioned in a second process to obtain the deep blue-coloured (reduced) state. High-throughput, large-area processing was demonstrated on a customized roll-to-roll pilot line with a coating width of up to 250 mm (Figure 2).

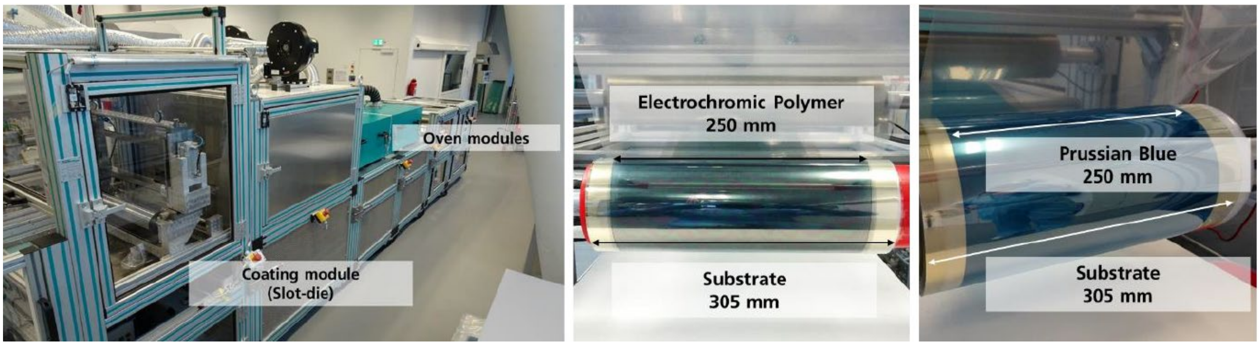

Figure 2: Roll-to-roll coating line for the production of the EC material (left) and photographic images of both EC electrodes (EC polymer, centre/Prussian blue, right).

Here, an EC polymer thin film on PET-ITO is used as the EC electrode combined with Prussian blue (PB) as the ion storage electrode [14]. Figure 3 displays the transmission spectra of the flexible EC elements (active area: 9 x 9 cm²) in the bright and dark states. The bright state (at +1.8 V) exhibits a highly transmissive, almost neutral tinted state with a visible light transmittance (τ_v) of 52%, whereas the dark state (at -1.4 V) is deep blue coloured with a τ_v value of 3%.

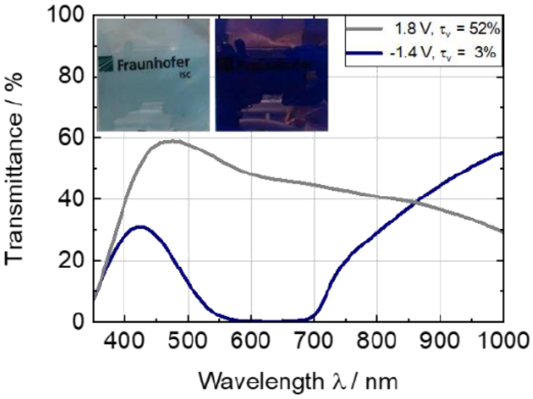

Figure 3: Transmission spectra and photographic images of the bright and dark states of the flexible EC element (EC polymer/PB).

Large-scale EC elements can be manufactured by either sheet-to-sheet (batch process) or roll-to-roll (continuous) processes. In general, sheet-to-sheet assembly of EC devices is more time-consuming, but also offers greater flexibility in terms of design freedom. For roll-to-roll processing of flexible EC films, the final design is ideally defined before coating the active materials. The EC element shows mechanical flexibility paired with unique optical properties to be attached to or integrated into camouflage technologies to cover or change its appearance in the VIS and the NIR wavelength range of the electromagnetic spectrum. The combined colour of the EC element and a selection of military colours (A-D) is shown in Table 1. The colours are indicated by the CIE L*a*b* colour coordinates. The L* value denotes the brightness and ranges from L* = 0 (black) to L* = 100 (white). The a* value characterizes the red (a* = 127) to green (a* = -128) axis. Accordingly, the b* value denotes the yellow (b* = 127) to blue (b* = -128) axis. The (0,0) point in the a*b* coordinate system represents a neutral grey.

Table 1: Overview of the CIE L*a*b* colour coordinates of four different military colours (A-D) in combination with a flexible EC element in its bright and coloured states, respectively.

		EC element	A	B	C	D
without EC element	L*		39.1	36.1	31.9	73.5
	a*		-4.9	-5.1	10.1	4.9
	b*		5.7	12.4	10.3	26.9
with EC element (bright state)	L*	57.7	21.2	18.8	17.0	41.8
	a*	-8.6	-7.1	-6.8	2.2	-4.7
	b*	-3.6	-0.5	3.0	1.2	10.0
with EC element (dark state)	L*	9.4	3.7	3.5	3.4	5.0
	a*	18.5	3.1	2.2	2.0	7.1
	b*	-36.8	-8.8	-5.9	-4.9	-19.4

A required property of EC elements is high cycling stability. It must be possible to switch several thousands of times between the differently coloured oxidation states without a significant change in voltage range, switching speed, and transmittance of the bright and coloured (or intermediate) states, and without defects occurring, such as delamination and non-uniform bleaching or colouring. The cycling stability of EC materials and elements can be evaluated by observing the loss of charge density or change in transmittance and colour upon repetitive electrochemical cycling (e.g., galvanostatic steps). Here, materials capable of maintaining over 95% of their initial charge density or optical modulation during the application of boundary cell voltages are deemed stable. Because high durability is crucial for products exposed to outdoor conditions, UV protection and encapsulation are highly important. Polymeric EC devices should ideally be fabricated and sealed/encapsulated under an inert atmosphere to prevent oxygen and moisture ingress [15], thus ensuring high cyclability and photostability [6]. Common sealant materials used for organic electronics are also applicable to EC devices to improve shelf-life and prevent electrolyte degradation, as well as solvent evaporation [16]. Figure 4 displays the fast response of approximately 5 seconds for both bleaching and colouring, as well as high cycling stability for 10,000 cycles, indicated by the same t_v value in the dark state and just a slight decrease in the bright state (52% →48%) under inert conditions (glovebox, H_2O, $O_2 < 5$ ppm).

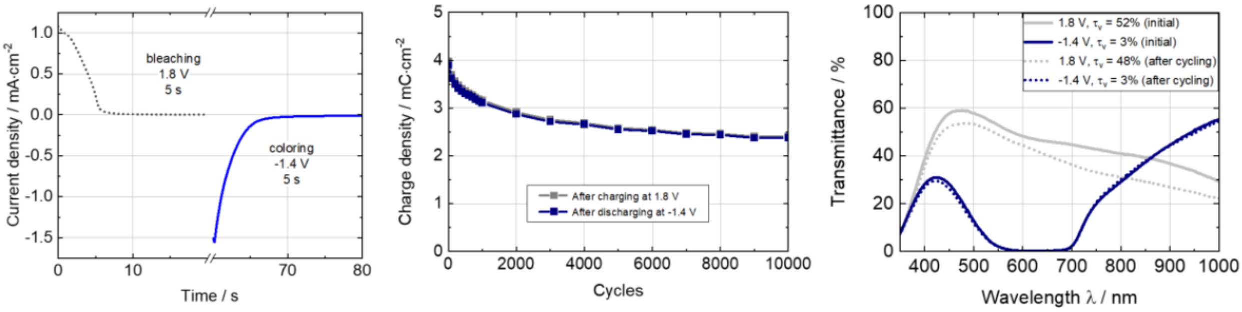

Figure 4: Electrochemical characterization (current density-time curves [left], electrochemical cycling (charge density, centre) and transmission spectra of the bright and dark states of the flexible EC element (EC polymer/PB) before and after the electrochemical cycling.

EC elements can be applied in camouflage in a number of ways, offering unique advantages over traditional camouflage technologies. One key advantage of polymeric EC materials and elements coated on flexible substrates is that they can conform to different surfaces and shapes. This means that they can be used in a wide range of applications, such as the following:

1) EC materials can be incorporated into clothing and equipment worn by military personnel, such as uniforms, backpacks, and helmets. Here, the materials can help the wearer blend into their surroundings and avoid detection.
2) For vehicles and buildings (e.g., tanks, airplanes, and command centres), EC materials can help these structures blend into their surroundings and avoid detection.
3) EC materials and elements can be used in displays, such as screens and signs, to create dynamic camouflage effects to blend into their surroundings or display messages or images that enhance situational awareness.

Lastly, electrochromics can be integrated into surveillance applications, such as drones or cameras, to be able to conduct surveillance operations more effectively.

4.0 CONCLUDING REMARKS

In conclusion, flexible EC elements based on an EC polymer on PET-ITO as the working electrode and Prussian blue on PET-ITO as the counter electrode, exhibits good EC properties in terms of colouration efficiency, optical contrast, transmission and colour neutrality in the bright state, and cycling stability (10,000 switching cycles) under lab conditions. The characterization of those multilayer assemblies demonstrates their visual uniformity and excellent functionality. Therefore, EC materials and elements offer a promising avenue for developing effective camouflage technologies, with a wide range of potential uses across military and civilian settings. This could provide a significant advantage for military personnel and vehicles, as they would be less visible to the enemy and better able to blend in with their environment. Overall, improving the stability of EC materials is a crucial step in developing novel camouflage technologies that can be used. By improving durability and robustness using accelerated aging tests, researchers can help to ensure that these materials can be used reliably over time, even in harsh environments.

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