

Review

Electrochromic Materials and Devices: Mechanisms, Emerging Technologies, and Applications

Vishu Sharma¹, Shifa Altaf¹, Neha Mittal¹, Neeraj Ravi¹, Mahima Koushik²
and Rakesh Kumar Soni^{1,*}

¹ Department of Chemistry, Chaudhary Charan Singh University, Meerut 250004, India

² Department of Chemistry, Gurukul Kangri, Deemed to be University, Haridwar 249404, India

* Correspondence: rksoni_rks@yahoo.com

How To Cite: Sharma, V.; Altaf, S.; Mittal, N.; et al. Electrochromic Materials and Devices: Mechanisms, Emerging Technologies, and Applications. *Environmental Guardian* **2026**, *1*(1), 4.

Received: 21 August 2026

Revised: 10 September 2026

Accepted: 14 September 2026

Published: 29 September 2026

Abstract: Electrochromic (EC) materials allow reversible and electrically controlled change of optical properties and are increasingly important in energy-efficient glazing, flexible electronics, sensing, and adaptive optics. This review critically examines recent advances in EC materials and devices with a focus on the relationships among materials selection, fabrication approach, switching mechanism, and device performance. Transition-metal oxides, metal complexes, conjugated polymers, and plasmonic metal/alloy systems are compared in terms of their optical contrast, coloration efficiency, response time, cycling stability, color tunability, and potential for large-scale manufacturing. Particular attention is paid to nanostructure engineering, compositional tuning, hybrid-device design, gel and solid electrolytes, and solution-processable approaches to large-area and flexible electrochromic devices. The opportunities and limitations of EC technologies are discussed in relation to the requirements of smart windows, flexible electronics, body-mounted sensors, and adaptive stealth systems. The key issues limiting the practical application of EC materials are the lack of long-term stability, electrolyte degradation, interfacial failure, limited multicolor tuning capability, high material costs in some systems, and scale-up challenges. Future directions of research and development will be determined by advances in materials chemistry, electrolyte and interfacial engineering, scalable fabrication approaches, accelerated lifetime testing under real-world conditions, and data-driven materials design. This review aims to provide an insight into the comparative advantages of different types of electrochromic materials and identify the directions for developing durable, high-performance, and cost-effective electrochromic devices, both at the materials level and device architecture.

Keywords: electrochromic materials; electrochromic devices; smart windows; tungsten trioxide; prussian blue analogs; conjugated electrochromic polymers; plasmonic nanostructures; flexible electrochromic devices; coloration efficiency

1. Introduction

Electrochromic (EC) materials are significant from the environmental perspective as they allow for dynamic management of sunlight and daylight exposure in buildings. When implemented in smart glass and building façade designs, EC devices can reversibly change the amount of visible light and the near-infrared radiation passing through the glass, thus, reducing unwanted heat gain in the summertime conditions while allowing the reception of useful solar energy and daylight. This ability to adapt is capable of decreasing the energy demand for cooling, heating, and lighting, providing improved visual and thermal comfort in indoor environment and lowering



Copyright: © 2026 by the authors. This is an open access article under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Publisher's Note: Scilight stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

maximum peak electricity load for operating buildings [1]. As a result of the fact that EC glazing reduces the operational energy use and minimizes greenhouse gas emissions during building operation, EC technologies should also have good durability, the right choice of materials, and have minimal energy demand for manufacturing [2]. Electrochromic (EC) materials, which reversibly change their optical properties under an applied electrical potential, have attracted intense research interest across four major material classes: transition-metal oxides, particularly WO_3 and NiO ; metal complexes, notably Prussian blue and its analogs; conjugated organic polymers; and plasmonic metal/alloy nanostructures. Polyoxometalates (POMs) are also important electrochromic materials and are discussed within the inorganic-material context because of their multielectron redox activity [3,4]. Each class offers a distinct combination of switching mechanism, color palette, fabrication route, and device performance characteristics, making the comparative evaluation of these material families within a unified framework essential for guiding the rational design of next-generation electrochromic devices (ECDs) [5].

Among the major EC material classes, conjugated electrochromic polymers warrant particular attention because their low cost, ease of processing, and structural tunability enable control of perceived color and other optical properties through blending, lamination, patterning, and copolymerization techniques [6–8]. Compared to their inorganic and small-molecule organic counterparts, EC polymers exhibit longer operational lifetimes, high optical contrast, stable oxidation states, excellent switching reproducibility, and mechanical flexibility, allowing them to be applied to non-planar, curved, or foldable surfaces [9,10]. More significantly, a variety of polymer architectures can produce distinct colors and access more than two redox states within a single device. Through these advantages, EC polymers are anticipated to find widespread application in thin-film transistors, OLEDs, optical shutters (smart windows, mirrors, sunglasses), variable-transmittance display devices, thermal-exposure indicators for frozen food packaging, EC printing, light intensity controllers, stealth coatings, probing of local potentials on biological cell membrane surfaces, and smart papers [11,12]. Materials for camouflage, spacecraft thermal control, and controllable light-reflective or light-transmissive optical data storage devices represent additional proposed application domains [13].

Several reviews have examined EC polymers with respect to their synthesis, properties, and applications. Prior works have individually covered conjugated polymers and their device fabrication [14], electrochromic conjugated polymers prepared by direct arylation polymerization [15], high-performance black copolymers for full visible-spectrum absorption [7], and transparent EC polymers with high optical contrast [16]. These reviews collectively confirm the significant and growing interest in EC polymeric materials driven by the expanding demand for new electrochromic device (ECD) concepts. However, due to the synthetic complexity of certain conjugated polymer systems, their limited thermal stability, and insufficient mechanical robustness, many of these polymers have not yet achieved commercial deployment [17]. The three most widely employed classes of EC materials in device fabrication are conjugated polymers (organic, Type III), metal oxide films (inorganic, Type III), and molecular dyes primarily viologen-based organic Type I materials [13]. Conjugated polymers have gained prominence over metal oxides and viologens owing to their low cost, ease of preparation, structural tunability, and flexibility [14,15]. Conjugated electrochromic polymers (ECPs) deliver substantial color versatility, high optical contrasts, rapid response times, and low power consumption during operation. Recent advances demonstrate optical contrasts exceeding 93% with cycling stability over 5000 cycles and less than 3% contrast decay [16]. Through systematic synthetic modifications, black-to-transparent copolymers that fully absorb the entire visible spectrum were designed by judiciously selecting four monomer types representing a landmark achievement in EC polymer design. The industrial demand for conjugated polymer-based ECDs continues to grow, driven by applications in automotive rearview mirrors, smart windows, aircraft optical shutters, reflective displays, and anti-glare sunglasses [10,11].

Polyamide (PA), polynorbornene (PNB), and polyimide (PI) represent a distinct class of high-performance polymers offering excellent mechanical properties and outstanding thermal stability. PIs and PAs are readily synthesized at low cost, Kapton® polyimide films (DuPont, Wilmington, DE, USA) and Kevlar® aramid fibers (DuPont, Wilmington, DE, USA) being among the most commercially prominent examples. PNBs such as Zeonex® (ZEON Corporation, Tokyo, Japan) and Arton® (JSR Corporation, Tokyo, Japan) are employed in precision optical applications owing to their high optical transparency. When functionalized with electroactive chromophores, these high-performance polymers become highly promising candidates for use in solid-state electrochromic devices (ECDs), combining fast EC response with long-term retention of electroactivity [12]. None of these EC polymers undergo a phase change from their solid-state during device operation, making them well-suited for all-solid-state ECD architectures [18]. Despite the wealth of individual reviews addressing specific subsets of EC materials such as conjugated polymers alone, metal oxides alone, or molecular dyes, a unified and critical examination encompassing all major EC material categories within a single comparative framework is absent from the current literature. Furthermore, rapidly emerging areas such as flexible and stretchable ECDs [9,10], dual-band

visible/near-infrared (VIS/NIR) modulation systems, multifunctional EC energy storage devices [11,12], and gel polymer electrolyte-based ECDs [18] have not been collectively addressed in prior reviews. The present review therefore aims to: (i) systematically categorize and critically evaluate EC materials across all major classes; (ii) compare their fabrication and processing strategies; (iii) benchmark key performance parameters including optical contrast ($\Delta T\%$), coloration efficiency (CE), switching time (t_c and t_b), and cycling stability across material categories; (iv) identify specific research gaps and unresolved challenges; and (v) provide concrete, forward-looking recommendations for future research and the commercialization of EC technologies. The literature surveyed spans primarily from 2016 to 2026, with inclusion of seminal foundational works where necessary for mechanistic context.

Although some past reviews have looked at types of electrochromic materials like metal oxides, conjugated polymers, molecular dyes or certain device setups there is still a need for a complete comparison across the four main groups of electrochromic materials. This review aims to show how the chemistry of the materials the way they are made how they switch the device setup and their performance are connected. The main new part of this review is the comparison framework. It looks at transition-metal oxides, metal complexes, conjugated polymers and plasmonic metal or alloy systems. It uses the standards to measure how well they perform, like how much color they can change, how efficient they are, how fast they switch how long they last how they can change color how flexible they are and how easy they are to make in large amounts. The studies used in this review are mostly from peer-reviewed papers published between 2016 and 2026. Some older important papers are also included when needed for background information. This review is about materials and devices that are useful for smart windows, flexible and wearable systems, biomedical sensing and other optical applications. It does not cover every type of molecular electrochromic dye or device setup that has been studied. Section 2 talks about improvements in applications. Section 3 looks at how they're made the types of materials how they switch and how they perform. Section 4 gives an overview of the techniques used to test them. Section 5 points out the problems and areas that need research. Section 6 gives ideas, about where the research might go. Section 7 has the thoughts.

2. Recent Advances in EC Material Design

The design and fabrication of high-performance electrochromic devices (ECDs) typically involve multilayer architectures comprising an EC active layer, ion storage layer, electrolyte, and transparent conducting electrodes. Recent research has focused on optimizing each component individually while simultaneously addressing system-level performance requirements such as switching speed, optical contrast, cycling stability, and scalability [11,17]. This section critically evaluates recent advances in EC materials and devices across four key application domains: smart windows, flexible and wearable ECDs, biomedical sensing, and stealth/defense applications.

2.1. Smart Windows and Energy-Efficient Glazing

Smart windows also referred to as switchable or dynamic glazing represent the most commercially mature application of EC technology. By dynamically modulating the transmission of solar radiation, EC smart windows can significantly reduce building energy consumption for both heating and air conditioning. Buildings lose approximately 45% of their energy through windows and facades, making the development of effective EC glazing a high-priority research area [19]. WO_3 -based inorganic ECDs remain the benchmark for large-area smart window applications due to their excellent cathodic EC performance, scalable thin-film deposition, and compatibility with glass substrates [20].

A particularly significant recent advancement is the development of dual-band EC smart windows, capable of independently controlling the transmission of visible (VIS) light and near-infrared (NIR) heat radiation. Dual-band electrochromic smart windows (DESWs) can operate in four distinct modes: “bright”, “cold”, “warm”, and “dark” corresponding to different combinations of VIS and NIR transmission states [19,21]. This level of spectral control goes far beyond what is achievable with conventional single-band EC systems and enables precise, season- and climate-adaptive regulation of indoor luminosity and thermal comfort. However, research on dual-band ECDs remains in an early stage, and significant challenges in switching speed, long-term stability, and device assembly must be overcome before commercial deployment.

A critical unresolved challenge in smart window ECDs particularly those using liquid electrolytes is electrolyte evaporation, leakage, and long-term degradation, which compromise both device performance and operational safety [18]. Solid and gel polymer electrolytes have emerged as the most promising alternatives, offering improved ionic conductivity, mechanical flexibility, and leak-proof operation. A comprehensive review of functionalized gel polymer electrolytes (GPEs) for ECDs has highlighted their applicability in smart windows, displays, and energy storage devices. Despite their advantages, GPEs currently suffer from lower ionic

conductivity compared to liquid electrolytes, particularly at low temperatures, and their long-term electrochemical stability under cycling remains a concern that warrants further investigation.

2.2. Flexible and Wearable Electrochromic Devices

The rapid growth of the Internet of Things (IoT), wearable health monitoring, and flexible display industries has placed new demands on ECD technology specifically, the need for devices that are mechanically compliant, lightweight, and compatible with curved or textile substrates [9]. Flexible ECDs (FECDs) represent a fundamentally different design paradigm from conventional rigid glass-based devices and require innovations at every layer of the device stack.

Recent progress in FECDs has been enabled by advances in three key areas: (i) flexible substrate materials (PET/ITO, silver nanowire networks, carbon nanotube films); (ii) low-dimensional EC active materials (WO_3 nanowires, V_2O_5 nanosheets) that maintain EC performance under mechanical deformation; and (iii) solid or gel polymer electrolytes that eliminate liquid handling while preserving ionic conductivity [9,10]. A notable development is the fabrication of electrochromic fibers yarns exceeding 100 m in length that can be woven directly into smart textiles for wearable color-changing displays [10].

Despite these advances, a critical limitation of current FECDs is the trade-off between mechanical flexibility and electrochemical performance. Flexible substrates with lower electrical conductivity than rigid ITO-glass introduce higher sheet resistance, which slows ion transport and increases switching times in large-area devices [9]. Furthermore, repeated mechanical deformation leads to delamination at the electrolyte/electrode interface, causing irreversible performance degradation over cycling, a challenge that remains insufficiently addressed in the literature. Roll-to-roll (R2R) fabrication, while theoretically viable, has not yet been demonstrated at production scale with adequate device yield, representing a critical gap between laboratory demonstrations and commercial realization.

2.3. Biomedical Sensing and Diagnostic Applications

EC materials have emerged as promising transducers for biomedical affinity sensors, leveraging the direct visual optical readout of electrochemical recognition events as a simple, instrument-free detection signal [17]. Conducting polymers particularly PEDOT:PSS, polypyrrole, and polyaniline derivatives are especially well-suited for this application due to their inherent biocompatibility, solution processability, and tunable redox properties [22]. When functionalized with biological recognition elements (antibodies, aptamers, enzymes), these EC polymers provide both the transduction and signal output functions within a single material layer.

An important emerging concept is the use of conducting EC polymers as “stealth coatings” for implantable biosensors, reducing the foreign body immune response and signal drift associated with long-term in vivo sensor operation [17]. The optical readout in such systems, a visible color change corresponding to a specific analyte concentration eliminates the need for complex electronic readout instrumentation, making EC-based sensors particularly attractive for resource-limited or point-of-care diagnostic settings. However, the sensitivity and selectivity of current EC affinity sensors remain inferior to established electrochemical and fluorescent biosensors, and the stability of the biorecognition layer under repeated electrochemical cycling is a critical unresolved challenge [22].

2.4. Stealth and Defense Applications

Electrochromic materials are increasingly being explored as intelligent adaptive stealth materials for defense applications, where dynamic control over surface appearance and thermal emittance is operationally critical [23]. Under an applied electric field, EC materials with multicolor switching capability can reversibly alter both their visible appearance and infrared (IR) emittance, enabling real-time adaptive camouflage that responds to changing background environments. This is a significant advancement over conventional passive camouflage materials, which offer no dynamic adaptability.

Recent research has demonstrated polymer/graphene oxide composite EC coatings (e.g., polythiophene/RGO/ Fe_3O_4) that simultaneously provide multicolor electrochromic switching and radar microwave absorption, enabling dual-function stealth performance against both optical and electronic detection [23]. However, critical limitations persist: most EC stealth demonstrations have been conducted under controlled laboratory conditions, and performance under operationally realistic conditions wide temperature ranges, mechanical stress, prolonged outdoor UV exposure has not been systematically evaluated. Furthermore, the switching speed of current EC stealth materials (typically 5–30 s) is insufficient for rapid adaptive camouflage in dynamic battlefield environments, representing a key research gap that must be addressed for practical deployment. A comparative

overview of the major electrochromic application domains, representative EC materials, key advantages, and current limitations is presented in Table 1.

Table 1. Comparative Overview of EC Application Domains.

Application Domain	Key EC Materials	Key Advantage	Main Limitation	References
Flexible/Wearable ECDs	Conjugated polymers, WO ₃ nanowires	Mechanical compliance, textile integration	Interface delamination, high sheet resistance	[9,10]
Biomedical Sensing	PEDOT:PSS, polypyrrole, PANI	Visual readout, biocompatibility	Lower sensitivity vs. fluorescent sensors	[17,22]
Smart Windows	WO ₃ , NiO, dual-band composites	Energy-efficient solar control	Slow switching, liquid electrolyte instability	[20,21]
Stealth/Defense	Polythiophene composites, metal oxides	Dual optical + radar stealth	Slow response, lacks outdoor durability data	[23]

3. EC Material Categories: Processing, Mechanisms, and Performance

3.1. Fabrication and Processing Techniques for Polymer-Based ECDs

The fabrication of polymer-based electrochromic devices (ECDs) relies on a range of solution-based and vapor-phase processing techniques that have been systematically optimized for film uniformity, scalability, and device performance [24]. The primary solution-based methods: spin coating, blade coating, spray coating, and inkjet printing offer versatility for depositing a broad range of conjugated EC polymers, including thiophene- and dioxythiophene-based ECPs in various colors. Notably, the charge storage layer which commonly employs pre-oxidized, minimally color-changing polymers such as PEDOT:PSS or polypyrrole can also be deposited using the same solution-based techniques as the EC active layer [24].

Spin coating produces films of highly uniform thickness by combining centrifugal force with rapid solvent evaporation. Key process parameters governing final film quality include rotational speed, spin duration, and solution viscosity. Studies have demonstrated that ECP films processed by spin coating exhibit superior volumetric redox activity compared to those processed by spray coating or blade coating, attributed to higher film density and improved morphological uniformity [24].

Blade coating achieves film uniformity through the controlled translational motion of a doctor blade across the substrate surface. Process variables including blade gap, coating speed, and substrate temperature collectively determine the final film thickness and morphology. Spray coating operates through atomization of the polymer ink at the spray nozzle, producing droplets that deposit onto the substrate upon impact. Uniformity of spray-coated films is governed by atomization pressure, nozzle-to-substrate distance, ink reservoir pressure, and spray pass overlap pattern. Careful optimization of these parameters enables large-area uniform coatings, as confirmed by transmittance measurements at multiple substrate positions. Inkjet printing uniquely enables the selective deposition of different ECPs onto distinct regions of a single substrate, making it the most suitable technique for multi-pixel, multicolor ECD fabrication [9]. In principle, dip coating is also applicable for ECP deposition; however, it requires additional processing steps to remove the coating from the non-conductive side of the substrate, limiting its practical utility.

In addition to solution-based methods, electrochemical polymerization (electrodeposition) is widely employed for *in situ* EC polymer film formation, particularly in Type II ECD architectures where the EC layer is grown directly on the electrode surface. This technique yields highly adherent, morphologically controlled polymer films with precisely tunable thickness governed by the applied charge density [15].

Roll-to-roll (R2R) processing is the critical pathway from laboratory-scale fabrication to industrial-scale ECD manufacturing. A key challenge in conventional R2R fabrication of ECDs has been the requirement for lamination of two independently coated electrodes, a discrete step that disrupts continuous processing. This limitation was overcome through a bottom-up fabrication approach utilizing UV-curable solid electrolytes, enabling fully integrated R2R processing without a separate lamination step [24]. Sotzing and coworkers demonstrated an important advance in which conducting polymer composites were synthesized by electrochemical polymerization directly within a pre-assembled solid-state polymer electrolyte matrix, enabling the large-scale fabrication of ECDs from soluble precursor polymers using the R2R process. The working principle and multilayer architecture of a typical complementary WO₃/NiO ECD, which forms the basis of most fabrication strategies discussed above, are illustrated schematically in Figure 1 [25].

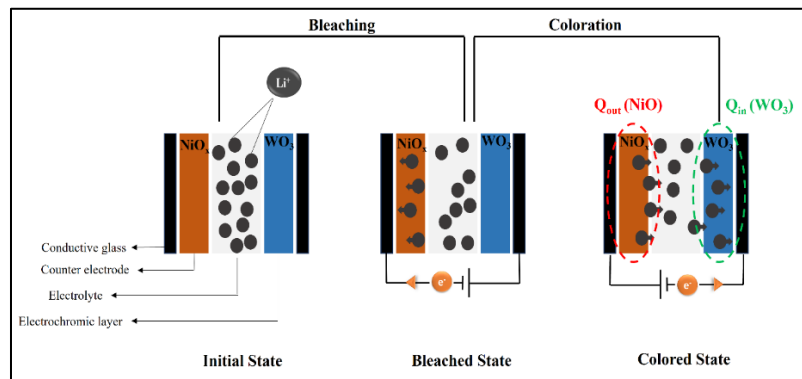


Figure 1. Schematic diagram illustrating the working principle of a complementary WO₃/NiO electrochromic device (ECD), showing Li⁺ ion insertion/extraction during the Initial, Bleached, and Colored states.

For display applications requiring spatial pixel definition, patterning of ECPs is essential alongside large-area coating. Investigated patterning techniques include photolithography, soft lithography, screen printing, and micro- and nano-imprinting. Photolithography achieves feature sizes below 1 μm through UV-crosslinking of ECP films; however, UV exposure under ambient moisture and oxygen can cause degradation of the ECP, necessitating inert atmosphere processing. Soft lithography and nano-imprinting circumvent this limitation by using a mechanical mold pressed onto the polymer film, shielding the ECP from UV exposure while generating the desired pattern. Contact printing, a technique previously applied to OLED and QD-LED device manufacturing has recently been demonstrated for ECD pixel patterning as a proof of concept, yielding switching behavior comparable to spray-coated reference devices.

3.2. EC Material Categories: Mechanisms and Performance

A. Metal Oxides (Transition Metal Oxides)

Tungsten trioxide (WO₃) is the most extensively studied cathodic EC material and remains the benchmark for inorganic ECD applications [26,27]. As an indirect bandgap semiconductor, WO₃ undergoes reversible ion intercalation and deintercalation accommodating H⁺, Li⁺, Na⁺, and K⁺ ions to generate the EC effect according to Equation (1):



where M = H, Li, Na, or K. Cathodic polarization drives metal ion insertion and simultaneous electron injection, reducing W⁶⁺ to W⁵⁺. Photon-mediated intervalence charge transfer (IVCT) between neighboring W⁵⁺ and W⁶⁺ sites produces an intense blue coloration at low x values. At higher x values, the blue H_xWO₃ phase transitions to a golden-red tungsten bronze as the lattice undergoes structural expansion and the tungsten center's oxidation state is progressively reduced. Although WO₃ films exhibit EC activity in aqueous electrolytes, dissolution of WO₃ in water especially in acidic electrolytes significantly impairs long-term durability and restricts compatible electrolyte choices [26].

A key figure of merit for EC devices is the coloration efficiency (CE), defined as the change in optical density (ΔOD) per unit charge density (Q, mC cm^{-2}) inserted or extracted, as given by Equation (2):

$$\text{CE} = \Delta\text{OD}/Q = \log(T_b/T_c)/Q \text{ (cm}^2 \text{ C}^{-1}\text{)} \quad (2)$$

where T_b and T_c are the bleached-state and colored-state transmittances, respectively. A higher CE value indicates larger optical modulation per unit charge, reducing energy consumption per switching cycle. Faster metal ion insertion kinetics, better long-term cycling stability, and higher CE are all favored by crystalline nanoparticles with smaller dimensions and shorter ion diffusion path lengths [27].

Several effective strategies have been developed to enhance the Electrochromic (EC) performance of WO₃. Nanostructuring: Crystallized porous WO₃ nanoparticles grown by hot wire chemical vapor deposition (HWCVD) and deposited electrophoretically on SnO₂:F-coated glass electrodes initially appeared blue and transitioned to fully transparent after 2 h of air annealing at 300 °C, demonstrating improved ion accessibility [27]. Composite formation: Honeycomb-structured WO₃/TiO₂ (90:10) films, fabricated by anodizing sputtered W/Ti films in fluorinated ethylene glycol, exhibited a 250% improvement in charge capacity and less than 1% transmittance at 800 nm in the colored state. The films also showed faster coloration and bleaching kinetics due to the more accessible TiO₂ framework [28]. Rare earth doping: Eu³⁺-doped WO₃ EC films exhibit bifunctional electrochromic switching combined with red photoluminescence along with a faster coloration response (7.2 s) and higher CE than undoped WO₃ films [29].

Transition metal doping: 1.5% Ni-doped WO₃ nanostructure-based EC films demonstrate enhanced cycling stability of up to 5500 cycles and color switching between transparent and deep blue states. At higher applied voltages, the device darkens to near-black state, resulting in a maximum transmission drop of 3.5%, which is useful for energy-efficient infrared-blocking smart windows [29]. Flexible substrate integration: RF plasma-sputtered WO₃ thin films (465 nm), combined with LiClO₄/PMMA/PC/ACN gel electrolytes on flexible PET substrates achieve switching times of $t_c = t_b = 5.88$ s with $\Delta T\% = 49\%$ at 1.6 V. Comparative studies confirm that gel electrolytes outperform liquid LiTRIF electrolytes due to shorter ionic transport path lengths, while aqueous LiClO₄ ($t_b = 8.71$ s, $t_c = 13.23$ s) outperforms non-aqueous LiTRIF ($t_b = 16.33$ s, $t_c = 20.8$ s) owing to its higher ionic conductivity [30]. Nickel oxide (NiO) functions as the complementary anodic EC material to cathodic WO₃. NiO transitions from a transparent bleached state to a colored state upon extraction of protons or insertion of OH[−] ions, as described in Equation (3):

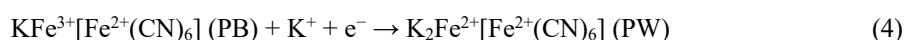


The bleached NiO film comprises a mixture of Ni hydroxide and oxide phases. NiO is preferred over iridium oxide (IrO₂) another anodic EC material due to the scarcity and high cost of iridium, which limit its scalability for large-area device fabrication [31]. Cathodic WO₃ and anodic NiO form an effective complementary electrode pair in dual-electrode ECDs, where both electrodes switch simultaneously under applied bias, achieving higher optical contrast and cycling reversibility than single-electrode configurations. A WO₃ (200 nm)/NiO (60 nm) complementary ECD demonstrated $\Delta T = 46\%$ at 633 nm, switching times of $t_c = 3.1$ s and $t_b = 4.6$ s, and 93% retention of initial ΔT after 2500 cycles highlighting the robustness of the complementary design [25].

B. Metal Complexes

Metal complexes employing redox-active metal centers coordinated to cyanide or other ligands constitute a well-established class of EC materials. Prussian blue (PB) iron(III) hexacyanoferrate(II) is among the oldest EC materials and uniquely accesses four distinct color states within a single device: transparent/colorless (Prussian White, PW) at 0.3 V, blue (PB) at 0.5 V, green (Berlin Green, BG) at 1.0 V, and yellow (Prussian Yellow, PY) at 1.7 V [32]. The key redox transitions governing these color states are:

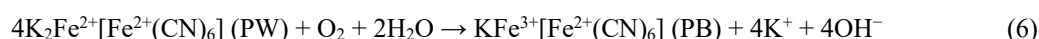
Equation (4)—Reduction (blue → colorless):



Equation (5)—Partial oxidation (blue → green):



Equation (6)—Spontaneous oxidation by dissolved O₂:



In PB/KCl electrolyte ECDs, applying a cathodic bias converts blue PB to colorless PW (Equation (4)). Upon removal of bias, dissolved oxygen spontaneously re-oxidizes PW back to PB (Equation (6)), or this recovery can be accelerated by applying a reverse anodic bias. A self-sustaining PB/aluminum ECD has been reported, where aluminum corrosion serves as the driving energy source for PB-to-PW conversion; however, the device's cyclability is inherently limited by the consumption of the sacrificial Al electrode, and net energy savings are questionable given the energy-intensive production of aluminum [32].

PB analogs synthesized by reacting transition metal salts (CoCl₂·6H₂O, CuSO₄·5H₂O, NiCl₂) with ferro/ferricyanide ions extend the accessible color palette significantly. A multicolor ECD using a PB/Ni-PBA working electrode and a Cu-PBA counter electrode on ITO substrates achieving blue (0.4 V), transparent yellow (1.0 V), and a mixed dark-red/blue state at intermediate potentials [33]. To enhance ion conductivity in PB-based EC films, multilayer assemblies of PB nanoparticles with organic poly(ethylenimine) (LPEI) have been reported to achieve switching times of $t_c = 5.5$ s and $t_b = 5.9$ s with strong optical contrast at 700 nm. More recently, homogeneous and nanogranular PB films were reported to deliver optical modulation of 80%, CE = 417.79 cm² C^{−1}, and remarkable cycling stability over 16,000 cycles currently among the best reported values for PB-based ECDs [32]. Three-dimensionally printed PB-viologen hybrid ECDs have also been demonstrated, illustrating the compatibility of PB analog systems with advanced manufacturing techniques [34].

A critical limitation of PB-based ECDs is their sensitivity to humid and alkaline environments, which cause structural decomposition of the PB lattice over extended cycling [32]. Furthermore, the recovery time of approximately 4 h in self-sustaining PB/Al devices without reverse bias is impractical for most applications, underscoring the need for improved PB stability and faster recovery strategies.

C. Metal Plasmonics: Metal/Alloy Materials

Metals and alloys serve as EC materials through three distinct mechanisms: (i) plasmonic absorption by noble metal nanoparticles via localized surface plasmon resonance (LSPR); (ii) reversible electrodeposition and dissolution of metal ions; and (iii) reversible hydrogen insertion and extraction in metal alloy films [35,36]. The LSPR phenomenon in which conduction electrons of metal nanoparticles smaller than the incident light wavelength undergo collective resonant oscillation produces vivid, spectrally narrow colors with high chromaticity, sub-micrometer pixel dimensions, and excellent photostability, making plasmonic nanostructures highly attractive for EC display applications [36].

A significant demonstration of electrically controlled LSPR tuning was reported using gold nanocubes (AuNCs) coated with electrochromic polyaniline (PANI) shells [35]. The PANI shell functions both as an electroactive medium enabling reversible optical-state switching under applied potential and as a controlled dielectric spacer between the AuNC core and the surrounding electrolyte. Electrochemical switching of the PANI oxidation state modulates the shell thickness and local refractive index, producing reversible and reproducible shifts in the primary LSPR peak with high electrochemical stability. In plasmonic EC systems, ions are adsorbed on the material surface rather than intercalated into a crystal lattice, circumventing lattice distortion and thereby delivering superior cycling stability compared to intercalation-based metal oxide EC systems [36].

Silver-based EC devices operate through reversible electrodeposition of Ag nanoparticles at the electrode surface (colored state) and their dissolution back into solution (bleached state). The use of a redox mediator accelerates bleaching by facilitating faster oxidative dissolution of the electrodeposited silver. However, faster dissolution compromises multicolor generation and long-term stability creating a fundamental trade-off between switching speed and device durability [35]. In the open-circuit state, silver-based ECDs spontaneously transition to the transparent state, irrespective of the presence of a redox mediator.

A critical limitation of plasmonic EC systems particularly those based on gold is their restricted scalability to large areas, since the nanometer-precision metal deposition required for LSPR control is incompatible with low-cost, large-area manufacturing processes [36]. The high cost of noble metals, while partly offset by the minimal quantities required for ultrathin nanostructures, remains a concern for commercial deployment. Furthermore, NIR-range plasmonic materials based on metal oxides, nitrides, and silicides exhibit suboptimal plasmonic absorption due to low-frequency interband transitions from partially filled d-states, restricting their effective EC color range in the NIR region. Table 2 presents a comprehensive benchmarking of key EC performance parameters across all major material classes discussed in this review, enabling direct cross-category comparison of coloration efficiency, optical contrast, switching speed, and cycling stability.

Table 2. Performance Benchmarking of EC Materials Across Major Material Classes.

Material Class	Representative Material	Synthesis Method	CE (cm ² C ⁻¹)	ΔT%	t _c (s)	t _b (s)	Cycling Stability	Ref
Metal Oxide	WO ₃ energy storage device	Sol-gel	101.2	82.3% @ 720 nm	2.9	5.7	—	[5]
Conjugated Polymer	Black-to-transparent copolymer	Direct arylation polymerization	1078	Full visible spectrum	—	—	—	[7]
Conjugated Polymer	Transparent ECP (high contrast)	Electrochemical polymerization	— ^a	>93%	—	—	<3% decay/5000 cycles	[16]
Metal Complex	Prussian blue (PB) nanogranular	Chemical co-precipitation	417.79	80% @ 700 nm	5.5	5.9	16,000 cycles	[32]
Metal Complex	PB/Ni-PBA + Cu-	Chemical precipitation	— ^a	Multicolor (blue/yellow/red)	—	—	—	[33]
Complex Plasmonic	PBA multicolor AuNC/PANI (eNPoM)	Seed-mediated synthesis	— ^b	~100 nm LSPR shift	<1	<1	>1000 cycles	[35]
Plasmonic Metal	Ag electrodeposition	Electrodeposition	— ^b	High chromaticity	<1	<1	Limited (trade-off) 93% retention/2500 cycles	[35]
Metal Oxide	WO ₃ /NiO complementary ECD	RF sputtering	90	46% @ 633 nm	3.1	4.6	—	[37]
Metal Oxide	WO ₃ flexible (gel electrolyte/PET)	RF plasma sputtering	— ^a	49% @ 1.6 V	5.88	5.88	— ^a	[38]
Metal Oxide	WO ₃ /TiO ₂ honeycomb composite	Anodization	— ^a	<1% T @ 800 nm	—	—	250% improved charge capacity	[39]
Metal Oxide	1.5% Ni-doped WO ₃	Hydrothermal	60.62	78.31%	—	—	25,000 cycles	[40]

—^a: Not reported in cited source. —^b: CE not applicable; plasmonic systems are characterized by LSPR peak shift (nm) rather than conventional charge-based coloration efficiency.

4. Characterization Techniques for Electrochromic Materials and Devices

Reliable characterization of EC materials and devices requires a coordinated suite of electrochemical, optical, and *in situ* analytical techniques. Together, these methods provide a comprehensive picture of switching mechanisms, performance metrics, degradation pathways, and device-level behavior information essential both for benchmarking materials and for guiding rational device design [17,41].

4.1. Cyclic Voltammetry (CV)

Cyclic voltammetry is the foundational electrochemical technique for characterizing EC materials. By sweeping the applied potential between defined anodic and cathodic limits at a fixed scan rate and recording the resulting current response, CV reveals: (i) the redox potentials at which EC switching is activated; (ii) the electrochemical reversibility of oxidation-reduction transitions, assessed by the ratio of anodic to cathodic peak currents ($I_{pa}/I_{pc} \approx 1$ for fully reversible systems); (iii) the number of accessible redox states within the electrochemical stability window; and (iv) the charge storage capacity of the EC active layer, directly correlated with optical contrast [4]. Scan-rate-dependent CV studies further discriminate between diffusion-controlled intercalation kinetics—where peak current scales with $v^{0.5}$ and surface-confined adsorption-controlled processes where peak current scales linearly with v , providing mechanistic insight that informs nanostructure geometry and electrolyte selection [42]. For conjugated EC polymers, CV additionally quantifies electroactive surface coverage and the onset and completion potentials of each colored state transition critical parameters for multicolor device design.

4.2. Chronoamperometry (CA) and Switching Kinetics

Chronoamperometry applies a step potential between the fully colored and fully bleached states and monitors the resulting current transient as a function of time. This is the standard method for quantifying EC switching kinetics specifically coloration time (t_c) and bleaching time (t_b), defined as the time required to achieve 90% of the maximum optical density change [41]. Integration of the CA current transient yields the consumed charge density (Q , mC cm^{-2}) per switching cycle, which feeds directly into the coloration efficiency (CE) calculation via Equation (2). Long-term cycling stability one of the most critical performance metrics for commercial EC applications is evaluated by repeating the CA square-wave switching protocol over thousands of cycles while tracking retention of $\Delta T\%$ and CE [17,43]. Deviations in the CA current profile shape over extended cycling, such as broadening of the current transient or loss of peak symmetry, serve as sensitive early indicators of ion trapping, electrolyte degradation, or interfacial delamination within the device.

4.3. UV-Vis Spectrophotometry and In Situ Spectroelectrochemistry

UV-Vis spectrophotometry measures the wavelength-dependent transmittance ($T\%$) of the EC film in its colored and bleached states, from which optical contrast ($\Delta T\%$) at the wavelength of maximum absorption is directly calculated the single most widely reported EC performance figure of merit [42]. *In situ* UV-Vis spectroelectrochemistry (SEC) extends this by coupling electrochemical potential control with simultaneous real-time optical monitoring, enabling: (i) complete mapping of the EC absorption spectrum across all accessible redox states; (ii) identification of intermediate colored states in multicolor EC systems such as Prussian blue analogs and conjugated polymers; (iii) calculation of CE from ΔOD vs. Q plots; and (iv) detection of spectral irreversibility and degradation during long-term cycling [4,44]. UV-Vis SEC is considered the method of choice for studying redox processes in EC materials, as it provides simultaneous electrochemical and molecular optical information under identical experimental conditions making it uniquely powerful for establishing structure-property relationships in new EC materials [44]. For dual-band smart window applications, spectroelectrochemical measurements must be extended into the NIR range (800–2500 nm) to fully capture the solar heat regulation performance of the EC device.

4.4. Electrochemical Impedance Spectroscopy (EIS)

EIS applies a small sinusoidal AC perturbation across a wide frequency range (typically 10 mHz–100 kHz) and measures the complex impedance response to deconvolute processes that are indistinguishable by DC techniques alone [17]. Fitting EIS data to an equivalent circuit model most commonly a modified Randles circuit incorporating a Warburg diffusion element yields quantitative values for: (i) bulk electrolyte ionic resistance; (ii) charge transfer resistance at the EC layer/electrolyte interface; (iii) solid-state ion diffusion coefficients within the EC active layer; and (iv) double-layer capacitance [4]. Tracking changes in these parameters before and after extended cycling provides a sensitive mechanistic probe of degradation in ECDs. For example, a progressive

increase in charge transfer resistance over cycling is diagnostic of interfacial passivation, while an increase in Warburg impedance suggests progressive ion trapping within the EC lattice both critical failure modes that EIS can distinguish without destructive device disassembly [41].

4.5. *In Situ and Advanced Characterization Techniques*

Beyond the standard electrochemical-optical suite, several advanced *in situ* techniques are employed to develop an atomic- and nanoscale mechanistic understanding of EC switching [4,44]. *In situ* X-ray diffraction (XRD) tracks real-time changes in lattice parameter in crystalline EC materials during ion insertion and extraction, providing direct structural evidence of phase transitions, lattice expansion, and intercalation-induced strain in WO₃ and Prussian blue systems [17]. *In situ* Raman spectroscopy, molecular-level structural changes are monitored in EC polymers and metal complexes during electrochemical cycling, detecting changes in conjugation length, bond character, and oxidation state that directly underpin EC color switching [44]. *In situ* dark-field spectroscopy is particularly valuable for plasmonic EC systems, enabling single-nanoparticle-level monitoring of LSPR peak shifts under an applied potential and providing direct nanoscale visualization of plasmonic tuning mechanisms [4]. Atomic force microscopy (AFM) measures the evolution of surface morphology and roughness in EC films before and after cycling, enabling visualization of crack formation, delamination, and morphological degradation at the nanoscale [42]. X-ray photoelectron spectroscopy (XPS) quantifies the oxidation-state distribution of metal centers, including W⁵⁺/W⁶⁺ in WO₃ and Fe²⁺/Fe³⁺ in Prussian blue, in both colored and bleached states, providing direct chemical evidence for EC switching mechanisms and identifying irreversible oxidation state changes associated with cycling degradation [17].

5. Challenges and Research Gaps

Despite the remarkable progress in EC materials and device engineering, several critical challenges continue to limit the commercial deployment and large-scale fabrication of ECDs. These challenges span material-specific limitations, device-level stability, and manufacturing scalability, and must be addressed systematically before electrochromic technologies can fully transition from laboratory demonstrations to real-world applications. A comparative overview of key EC materials, their synthesis methods, and limitations is presented in Table 3.

5.1. *Metal Oxide EC Materials*

Metal oxide-based EC devices offer a well-established advantage of low-voltage operation and low electrical energy consumption, making them highly attractive for energy-efficient smart windows and building-integrated applications [45]. However, the inherently large bandgap of most transition metal oxides results in poor electrical conductivity, which impedes efficient charge transport between the transparent conducting layer and the EC active layer a bottleneck that directly degrades switching speed and coloration efficiency [45]. Furthermore, conventional intercalation-based inorganic EC materials are severely limited in multicolor capability: because optical modulation depends on bulk ion insertion and extraction, achieving full-color tunability with closely adjacent wavelengths is extremely difficult using a single metal oxide material [46].

Polyoxometalate (POM)-based metal oxide materials exhibit stable EC switching responses due to their ability to function as multi-electron reservoirs without structural change; however, their poor solubility in common electrolytes and inadequate structural stability in solution environments prevent their integration into large-area devices [47]. Doping of metal oxides with aliovalent ions such as Eu³⁺, Ni²⁺, Mo⁶⁺, or Ti⁴⁺ has therefore emerged as a necessary strategy to simultaneously narrow the bandgap, improve electrical conductivity, and optimize nanostructure morphology for enhanced ion intercalation-deintercalation kinetics [40,48]. Nevertheless, a persistent challenge is the brittleness of metal oxide thin films, which limits their integration into flexible and wearable ECD platforms that require mechanical bendability without cracking or delamination [4,11].

5.2. *Metal Complex EC Materials*

Metal complexes particularly Prussian blue (PB) and its analogs (PBAs) offer a unique advantage in multicolor EC performance, enabling access to four distinct color states (colorless, blue, green, yellow) within a single material [32]. The distinctive redox-rich characteristics of PB and its transition metal analogs (Co-PBA, Cu-PBA, Ni-PBA) make PB-based ECDs a promising research direction for decorative patterns and multicolor displays [34]. However, PB-based ECDs suffer from severe sensitivity to humid and alkaline environments, leading to structural decomposition of the PB lattice over extended cycling. The slow spontaneous regeneration time of approximately 4 h in PB/Al self-sustaining devices makes them impractical for most responsive applications. Ion-

trapping and charge mismatch between complementary EC and counter electrodes further reduce cycling stability a fundamental challenge that remains unresolved in most complementary ECD configurations [37].

5.3. Organic and Polymer-Based EC Materials

Conjugated EC polymers (ECPs) offer superior color diversity, solution processability, and faster switching speeds compared to inorganic counterparts; however, their long-term electrochemical stability remains significantly inferior [49]. The imperfect spectral purity of ECPs caused by broad, overlapping absorption bands continues to limit their suitability for high-resolution, full-color display applications where precise wavelength selectivity is essential [5]. In addition, organic-inorganic hybrid EC systems which combine metal oxides or coordination complexes with organic polymers to balance the performance limitations of each individual material class face persistent challenges of insufficient film-forming ability, interface delamination, and long-term chemical incompatibility between the organic and inorganic components [50].

5.4. Hybrid EC Systems and Scalability

Hybrid EC systems that integrate different material categories such as polymer/metal oxide composites, viologen/MnO₂ assemblies, and plasmonic/polymer core-shell architectures represent a promising strategy for surpassing the performance ceiling of any single EC material class [51]. However, the key challenges facing hybrid systems are: (i) stability under prolonged electrochemical cycling, (ii) scalability for large-area fabrication, and (iii) cost-effective, reproducible synthesis routes compatible with industrial processing [45]. Cyclic performance degradation in ECDs arises from three primary mechanisms: structural damage to the EC active layer, irreversible side reactions within the electrolyte, and ion trapping at the electrode-electrolyte interface all of which require targeted materials engineering solutions [52].

Furthermore, the availability of renewable energy sources and the cost of electrical power directly constrain the practical deployment of ECDs in energy management applications, particularly in regions where electricity prices are high or grid access is unreliable. Addressing this challenge requires the integration of ECDs with photovoltaic or triboelectric energy harvesting systems to create self-powered smart windows an area of growing research interest but still limited maturity [11].

Table 3. Overview of Key EC Materials.

S.No	EC Material	Method of Synthesis	Description	Key Limitation	Reference
1	Nafion membrane	Commercial (solution cast)	Commercially available proton-exchange polymer electrolyte membrane used in solid-state ECDs	Complex processing and longer fabrication time; limited transparency modulation range	[5]
2	Prussian blue (PB)	Electrochemical deposition	Four-color-state inorganic complex (PW/PB/BG/PY) with high optical contrast and multicolor switching	Structural degradation in humid/alkaline environments; slow spontaneous color recovery (~4 h)	[32]
3	WO ₃ /TiO ₂ composite	Sol-gel/anodization	Transparent, proton-conducting metal oxide EC film with nanostructured honeycomb morphology	Limited charge storage layer options; brittleness incompatible with flexible substrates	[40,48]
4	PANI/polythiophene	Electrochemical polymerization	Conjugated EC polymer with high color contrast; potential for flexible and wearable ECD applications	Poor long-term electrochemical stability; spectral purity limitations restrict full-color display performance	[45]
5	WO ₃ Fabry-Pérot nanocavity	RF sputtering	Asymmetric reflective nanocavity enabling full-color tunability (red, yellow, green) via WO ₃ thickness control	Requires precise nanometer-scale thickness control; challenging large-area uniformity	[46]
6	PEDOT:PSS	Chemical oxidative polymerization	Highly transparent thermoplastic film used as solid electrolyte and charge storage layer in ECDs	Limited color palette (blue/gray); incomplete spectral coverage for full-color displays	[49]
7	Silk fibroin polymer	Chemical oxidative method	Natural animal-protein-derived polymer used to fabricate flexible solid electrolytes with biocompatibility	Poor interfacial contact between substrate and EC layer limits heterogeneous electron transfer; requires improved film-forming techniques	[50]
8	Viologen/ α -MnO ₂ hybrid	Electrochemical deposition + drop-casting	Inorganic-organic hybrid ECD combining fast-switching viologen with charge-dense MnO ₂ for enhanced performance	Stability under prolonged cycling; scalability of hybrid processing	[51]

6. Future Perspectives

The rapid evolution of EC materials and devices over the past decade has established a strong scientific foundation; however, several transformative research directions must be pursued to bridge the gap between laboratory-scale demonstrations and real-world industrial deployment. The following six future perspectives are identified as the highest-priority areas for advancing electrochromic technology.

The conventional trial-and-error approach to EC material and device optimization is time-consuming, resource-intensive, and inherently limited in exploring vast compositional and processing parameter spaces. Machine learning (ML) offers a powerful alternative by enabling data-driven prediction and optimization of EC performance metrics including $\Delta T\%$, CE, switching speed, and cycling life directly from electrochemical training datasets [53]. A landmark demonstration of this approach used a multilayer perceptron (MLP) model trained on cyclic voltammetry current density data to guide the fabrication of an inorganic all-liquid EC device, yielding $\Delta T = 74\%$, $t_c = 6.5$ s, $t_b = 13.5$ s, and >1000 cycle stability in a single optimized iteration, a result that would have required extensive empirical screening without ML guidance [53]. Broader integration of ML with high-throughput synthesis and combinatorial screening of EC polymer libraries, metal oxide dopant profiles, and electrolyte formulations represents a paradigm shift toward rational, accelerated EC material discovery [54]. AI-driven design platforms that couple density functional theory (DFT) calculations with ML models for predicting electronic structure-property relationships in novel EC materials are also emerging as powerful tools for pre-screening candidate compounds before synthesis [54].

A critical barrier to the widespread adoption of ECDs in portable, wearable, and building-integrated applications is their dependence on external electrical power sources. The integration of ECDs with photovoltaic cells, triboelectric nanogenerators (TENGs), piezoelectric energy harvesters, or galvanic redox cells to create fully self-powered smart windows and wearable EC textiles represents a compelling solution that simultaneously addresses energy consumption and autonomous operation requirements [10,55]. Self-powered EC sensors combining energy harvesting, EC visual readout, and signal transduction in a single platform are particularly promising for wearable health monitoring applications, including non-invasive sweat analysis and real-time physiological parameter display [10]. Future work must focus on improving the power conversion efficiency of integrated energy harvesting components under indoor low-irradiance conditions and ensuring long-term electrochemical compatibility between the energy source and the EC active layer over thousands of charge-discharge cycles.

Mechanical failure primarily crack propagation, delamination of EC active layers from substrates, and electrolyte fracture is the dominant degradation mode in flexible and wearable ECDs subjected to repeated bending, twisting, and stretching [56]. The development of intrinsically self-healing polymer electrolytes and EC active layers that autonomously repair mechanical damage through dynamic covalent bond reformation, hydrogen bonding networks, or reversible coordination chemistry would dramatically extend device operational lifetime without the need for external repair or replacement [52]. Hydrogel-based electrolytes incorporating self-healing moieties have recently demonstrated the ability to maintain ionic conductivity and mechanical integrity after multiple cut-and-heal cycles, making them strong candidates for next-generation flexible ECD electrolytes [43]. Achieving self-healing functionality without compromising optical transparency, electrochemical stability window, or ionic conductivity remains the central design challenge in this direction.

The realization of true full-color (red-green-blue, RGB) modulation in a single ECD platform essential for high-resolution reflective displays, adaptive camouflage, and decorative smart surfaces remains one of the most technically demanding open problems in EC research [5,46]. Current approaches being pursued include: (i) plasmonic nanostructure geometry engineering to shift LSPR absorption across the visible spectrum; (ii) Fabry-Pérot optical cavity design using precisely controlled WO_3 nanocavity thicknesses to generate structural colors across red, yellow, and green; and (iii) hybridization of complementary EC chromophores with non-overlapping absorption bands into a single dual- or multi-layer device [35,46]. A key challenge is that most multicolor EC systems require multiple independent electrode segments or stacked device layers increasing fabrication complexity and reducing device transparency in the bleached state. Future efforts should focus on developing single-layer, single-material systems with electrically switchable multi-wavelength absorption capability, ideally compatible with R2R processing.

Transitioning EC device fabrication from batch-mode laboratory processes to fully continuous R2R manufacturing is the single most important step toward cost-competitive, large-area commercial ECDs for smart window and display markets [24,43]. The recent development of bottom-up, lamination-free R2R ECD fabrication using UV-curable solid polymer electrolytes has demonstrated the technical feasibility of this approach; however, critical engineering challenges including maintaining film thickness uniformity across meter-scale substrate

widths, preventing pinhole defects during high-speed coating, achieving precise electrode alignment, and ensuring consistent optical and electrochemical performance across the full device area must be systematically addressed at pilot scale before commercial deployment [10,24]. The development of flexographic and gravure printing-compatible EC ink formulations with precisely engineered rheological properties represents a particularly important enabling technology for cost-effective R2R ECD manufacturing [57].

Achieving the tens of thousands of switching cycles required for commercial smart window and display applications while maintaining performance under variable outdoor temperature ($-20\text{ }^{\circ}\text{C}$ to $+80\text{ }^{\circ}\text{C}$), humidity (0–100% RH), and UV radiation conditions requires a fundamentally deeper mechanistic understanding of EC material degradation pathways [43,45]. The three primary degradation mechanisms irreversible ion trapping within the EC lattice, oxidative decomposition of the electrolyte at high applied voltages, and interfacial delamination between EC layer and TCO electrode must each be addressed through targeted material engineering strategies [45,52]. Promising approaches include: atomic layer deposition (ALD) of ultrathin protective interfacial coatings on EC active layers; design of wide electrochemical window ionic liquid and solid polymer electrolytes resistant to oxidative decomposition; and development of lattice-matched buffer layers that suppress ion trapping in metal oxide EC films. Standardized real-world accelerated aging test protocols directly comparable between different research groups and industrial standards are urgently needed to enable meaningful benchmarking of EC device stability across the field [43].

7. Conclusions

This review has provided a comprehensive examination of the major classes of electrochromic (EC) materials transition metal oxides and polyoxometalates (POMs), metal complexes (Prussian blue and its analogs), organic conjugated polymers (ECPs), and metal/alloy-based plasmonic systems encompassing their fabrication methods, working mechanisms, device performance metrics, and key limitations. Across all material categories, significant advancements have been achieved in coloration efficiency (CE), optical contrast ($\Delta T\%$), switching speed, and cycling durability over the past decade, driven by innovations in nanostructure engineering, heteroatom doping, hybrid material design, and solution-based processing techniques compatible with large-area and flexible substrate fabrication.

Among inorganic EC materials, nanostructured and doped WO_3 particularly in complementary WO_3/NiO dual-electrode device configurations remains the most technologically mature system for smart window applications, offering low operating voltage, high optical contrast, and reliable long-term cycling stability. Furthermore, dual-band electrochromic smart windows capable of independently modulating visible and near-infrared radiation represent an emerging frontier for season-adaptive, energy-efficient building glazing. Metal complex systems, especially Prussian blue and its transition metal analogs, uniquely enable multicolor EC performance within a single material platform, though their sensitivity to humid and alkaline environments and slow spontaneous color recovery remain persistent challenges. Organic ECPs offer unmatched color diversity and solution processability; however, their inferior long-term electrochemical stability and broad spectral absorption continue to limit their suitability for precision display applications. Plasmonic metal nanoparticle systems particularly PANI-coated gold nanocubes and silver-based reversible electrodeposition systems demonstrate exceptional color saturation and sub-micrometer pixel dimensions via LSPR tuning, but their scalability to large areas and cost competitiveness require further development.

From a manufacturing perspective, the maturation of solution-based processing techniques including spin coating, spray coating, inkjet printing, and UV-curable electrolyte-enabled lamination-free R2R fabrication has meaningfully narrowed the gap between laboratory-scale ECD demonstrations and industrial production. Hybrid EC systems that strategically combine organic and inorganic material components into a single device architecture have shown the potential to simultaneously overcome the color limitations of metal oxides and the stability limitations of organic polymers. The integration of ECDs with photovoltaic and triboelectric energy harvesting units to create fully self-powered smart windows represents a particularly high-priority research direction. Nevertheless, achieving the performance benchmarks required for commercial deployment including operation across tens of thousands of switching cycles under real-world outdoor conditions, electrolyte stability at the higher voltages required for large-area TCO-glass substrates, and cost-effective scalable fabrication remains the central challenge for the field. Continued interdisciplinary research integrating advanced materials chemistry, device engineering, and emerging computational design tools such as machine learning will be essential to accelerate the transition of electrochromic technology from promising laboratory demonstrations to transformative commercial applications in energy-efficient smart buildings, adaptive displays, wearable health-monitoring platforms, biomedical point-of-care sensors, and next-generation adaptive stealth and defense coatings.

Author Contributions

V.S.: Writing—original draft, methodology, preparation of figures and tables, visualized the study, writing—review and editing. S.A.: Writing—original draft, investigated the study, literature survey, data collection. N.M.: Investigated the study, literature survey, data collection. M.K.: Writing—original draft, investigated the study, literature survey, data collection. N.R.: Investigated the study, literature survey, data collection. R.K.S.: Supervision, Conceptualization, Validation. All authors have read and agreed to the published version of the manuscript.

Funding

This research received no external funding.

Institutional Review Board Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

No new data were created or analyzed in this study. Data sharing is not applicable as this article is a review of published literature.

Conflicts of Interest

Given the role as Journal Editor, Prof. Rakesh Kumar Soni had no involvement in the peer review of this paper and had no access to information regarding its peer-review process. Full responsibility for the editorial process of this paper was delegated to another editor of the journal.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

References

1. Granqvist, C.G.; Arvizu, M.A.; Bayrak Pehlivan, İ.; et al. Electrochromic materials and devices for energy efficiency and human comfort in buildings: A critical review. *Electrochim. Acta* **2018**, *259*, 1170–1182. <https://doi.org/10.1016/j.electacta.2017.11.169>.
2. Syrrakou, E.; Papaefthimiou, S.; Yianoulis, P. Environmental assessment of electrochromic glazing production. *Sol. Energy Mater. Sol. Cells* **2005**, *85*, 205–240. <https://doi.org/10.1016/j.solmat.2004.03.005>.
3. Mortimer, R.J. Electrochromic Materials. *Annu. Rev. Mater. Res.* **2011**, *41*, 241–268. <https://doi.org/10.1146/annurev-matsci-062910-100344>.
4. Ahmed, T.; Mazumder, A.; Kuriakose, S.; et al. Materials, mechanisms, and emerging applications of electrochromic systems. *Nanoscale* **2025**, *17*, 18049–18076. <https://doi.org/10.1039/d4nr02098g>.
5. Gu, C.; Jia, A.B.; Zhang, Y.M.; et al. Emerging Electrochromic Materials and Devices for Future Displays. *Chem. Rev.* **2022**, *122*, 14679–14721. <https://doi.org/10.1021/acs.chemrev.1c01055>.
6. Carbas, B.B.; Yildiz, H.B. A review of dithieno [3,2-b:2',3'-d]pyrrole-based electrochromic conjugated polymers. *Eur. Polym. J.* **2024**, *204*, 112700. <https://doi.org/10.1016/j.eurpolymj.2023.112700>.
7. Chen, D.; Tong, Z.; Rao, Q.; et al. High-Performance Black Copolymers Enabling Full Spectrum Control in Electrochromic Devices. *Nat. Commun.* **2024**, *15*, 8457. <https://doi.org/10.1038/s41467-024-52430-2>.
8. Liu, Q.; Yang, L.; Ling, W.; et al. Organic electrochromic energy storage materials and device design. *Front. Chem.* **2022**, *10*, 1001425. <https://doi.org/10.3389/fchem.2022.1001425>.
9. Wu, W.; Lee, P.S. Flexible and stretchable electrochromic displays: Strategies, recent advances, and prospects. *Soft Sci.* **2024**, *4*, 29. <https://doi.org/10.20517/ss.2024.21>.
10. Fan, Q.; Bai, Z.; Bao, B.; et al. Flexible electrochromic devices for wearable electronics. *Wearable Electron.* **2025**, *2*, 171–214. <https://doi.org/10.1016/j.wees.2025.05.001>.
11. Yu, X.; Guo, P.; Chen, J.; et al. Recent advances in multifunctional electrochromic devices. *Responsive Mater.* **2024**, *2*, e20240013. <https://doi.org/10.1002/rpm.20240013>.

12. Manjakkal, L.; Pereira, L.; Kumi Barimah, E.; et al. Multifunctional flexible and stretchable electrochromic energy storage devices. *Prog. Mater. Sci.* **2024**, *142*, 101244. <https://doi.org/10.1016/j.pmatsci.2024.101244>.
13. Yaseen, M.; Khattak, M.A.K.; Khan, A.; et al. State-of-the-art electrochromic thin films devices, fabrication techniques and applications: A review. *Nanocomposites* **2024**, *10*, 1–40. <https://doi.org/10.1080/20550324.2023.2291619>.
14. Neo, W.T.; Ye, Q.; Chua, S.J.; et al. Conjugated polymer-based electrochromics: Materials, device fabrication and application prospects. *J. Mater. Chem. C* **2016**, *4*, 7364–7376. <https://doi.org/10.1039/c6tc01150k>.
15. Wu, C.; Chen, H.; Lin, K.; et al. Recent advances in electrochromic conjugated polymers prepared by direct (hetero) arylation polymerization. *Synth. Met.* **2024**, *306*, 117632. <https://doi.org/10.1016/j.synthmet.2024.117632>.
16. Wang, Z.; You, L.; Pandit, V.; et al. Transparent Electrochromic Polymers with High Optical Contrast and Contrast Ratio. *JACS Au* **2024**, *4*, 2291–2299. <https://doi.org/10.1021/jacsau.4c00254>.
17. Chen, D.; Chua, M.H.; He, Q.; et al. Multifunctional electrochromic materials and devices recent advances and future potential. *Chem. Eng. J.* **2025**, *503*, 157820. <https://doi.org/10.1016/j.cej.2024.157820>.
18. Xu, L.; Zhang, L.; Liu, D.; et al. A Comprehensive Review of the Functionalized Integrated Application of Gel Polymer Electrolytes in Electrochromic Devices. *Nano-Micro Lett.* **2026**, *18*, 106. <https://doi.org/10.1007/s40820-025-01909-8>.
19. Wang, J.; Wang, Z.; Zhang, M.; et al. Toward Next-Generation Smart Windows: An In-depth Analysis of Dual-Band Electrochromic Materials and Devices. *Adv. Opt. Mater.* **2024**, *12*, 2302344. <https://doi.org/10.1002/adom.202302344>.
20. Qin, L.; Liu, Y.; Long, M.; et al. Advancements in dual-band electrochromic smart windows: Exploring single-component materials for sustainable building solutions. *Ceram. Int.* **2024**, *50*, 22174–22183. <https://doi.org/10.1016/j.ceramint.2024.03.380>.
21. Sun, F.; Pal, R.; Eom, S.Y.; et al. Fast-switching dual-cathode electrochromic smart windows for year-round building energy savings. *Nat. Commun.* **2025**, *16*, 9569. <https://doi.org/10.1038/s41467-025-64962-2>.
22. Ramanavicius, S.; Jagminas, A.; Ramanavicius, A. Advances in Molecularly Imprinted Polymers Based Affinity Sensors (Review). *Polymers* **2021**, *13*, 974. <https://doi.org/10.3390/polym13060974>.
23. Ahmadian-Alam, L.; Jahangiri, F.; Mahdavi, H. Fabrication and assessment of an electrochromic and radar-absorbent dual device based on the new smart polythiophene-based/RGO/Fe₃O₄ ternary nanocomposite. *Chem. Eng. J.* **2021**, *422*, 130159. <https://doi.org/10.1016/j.cej.2021.130159>.
24. Wang, H.; Barrett, M.; Duane, B.; et al. Materials and processing of polymer-based electrochromic devices. *Mater. Sci. Eng. B* **2018**, *228*, 167–174. <https://doi.org/10.1016/j.mseb.2017.11.016>.
25. Chen, P.W.; Chang, C.T.; Ko, T.F.; et al. Fast response of complementary electrochromic device based on WO₃/NiO electrodes. *Sci. Rep.* **2020**, *10*, 8430. <https://doi.org/10.1038/s41598-020-65191-x>.
26. Zheng, J.Y.; Sun, Q.; Cui, J.; et al. Review on recent progress in WO₃ -based electrochromic films: Preparation methods and performance enhancement strategies. *Nanoscale* **2023**, *15*, 63–79. <https://doi.org/10.1039/d2nr04761f>.
27. Yao, Y.; Sang, D.; Zou, L.; et al. A Review on the Properties and Applications of WO₃ Nanostructure-Based Optical and Electronic Devices. *Nanomaterials* **2021**, *11*, 2136. <https://doi.org/10.3390/nano11082136>.
28. Gu, H.; Tan, M.; Wang, T.; et al. Boosting the electrochromic performance of P-doped WO₃ films via electrodeposition for smart window applications. *RSC Adv.* **2024**, *14*, 10298–10303. <https://doi.org/10.1039/d4ra00979g>.
29. Bai, J.; Zhang, Y.; Pan, Z.; et al. Optimization of electrochromic Mo doping WO₃ films: A study on dual-phase stacked structures for energy-efficient smart windows. *Electrochim. Acta* **2024**, *508*, 145295. <https://doi.org/10.1016/j.electacta.2024.145295>.
30. Song, K.; Cao, Z.; Weng, S.; et al. Extraordinarily fast response all-solid-state electrochromic devices. *Sol. Energy Mater. Sol. Cells* **2024**, *278*, 113193. <https://doi.org/10.1016/j.solmat.2024.113193>.
31. Cheng, B.; Cao, Z.; Liao, L.; et al. Long-term stable quasi-solid-state complementary WO₃–NiO electrochromic devices with ultra-fast response. *Mater. Today Chem.* **2025**, *43*, 102471. <https://doi.org/10.1016/j.mtchem.2024.102471>.
32. Fu, X.; Li, K.; Zhang, C.; et al. Homogeneous and Nanogranular Prussian Blue to Enable Long-Term-Stable Electrochromic Devices. *ACS Appl. Mater. Interfaces* **2024**, *16*, 17745–17756. <https://doi.org/10.1021/acsami.3c17551>.
33. Liao, T.C.; Chen, W.H.; Liao, H.Y.; et al. Multicolor electrochromic thin films and devices based on the Prussian blue family nanoparticles. *Sol. Energy Mater. Sol. Cells* **2016**, *145*, 26–34. <https://doi.org/10.1016/j.solmat.2015.08.004>.
34. Thai, L.H.; Nhi, L.T.T.; Giang, T.C.; et al. 3D printed multicolor Prussian blue-viologen hybrid electrochromic devices: Toward high contrast ratio and fast switching electrochromic devices. *Appl. Mater. Today* **2024**, *40*, 102369. <https://doi.org/10.1016/j.apmt.2024.102369>.
35. Kim, Y.; Cha, S.; Kim, J.H.; et al. Electrochromic response and control of plasmonic metal nanoparticles. *Nanoscale* **2021**, *13*, 9541–9552. <https://doi.org/10.1039/d1nr01055g>.
36. Liu, Y.; Huang, L.; Cao, S.; et al. Plasmonic-based electrochromic materials and devices. *Nanophotonics* **2024**, *13*, 155–172. <https://doi.org/10.1515/nanoph-2023-0832>.
37. Ke, Y.; Wang, Z.; Xie, H.; et al. Long-Term Stable Complementary Electrochromic Device Based on WO₃ Working Electrode and NiO-Pt Counter Electrode. *Membranes* **2023**, *13*, 601. <https://doi.org/10.3390/membranes13060601>.

38. Eren, E.; Karaca, G.Y.; Koc, U.; et al. Electrochromic characteristics of radio frequency plasma sputtered WO₃ thin films onto flexible polyethylene terephthalate substrates. *Thin Solid Film*. **2017**, *634*, 40–50. <https://doi.org/10.1016/j.tsf.2017.05.009>.
39. Reyes-Gil, K.R.; Stephens, Z.D.; Stavila, V.; et al. Composite WO₃/TiO₂ Nanostructures for High Electrochromic Activity. *ACS Appl. Mater. Interfaces* **2015**, *7*, 2202–2213. <https://doi.org/10.1021/am5050696>.
40. Ahmad, K.; Kim, H. Fabrication of Nickel-Doped Tungsten Trioxide Thin Film-Based Highly Stable Flexible Electrochromic Devices for Smart Window Applications. *ACS Sustain. Chem. Eng.* **2023**, *11*, 10746–10754. <https://doi.org/10.1021/acssuschemeng.3c01483>.
41. Marciel, A.; Borges, J.; Pereira, L.; et al. Advancements in Electrochromic Technology for Multifunctional Flexible Devices. *Materials* **2025**, *18*, 2964. <https://doi.org/10.3390/ma18132964>.
42. Tan, M.Y.; Thien, G.S.H.; Tan, K.B.; et al. Investigation of electrochromic performances of multicolor V₂O₅ devices fabricated at low processing temperature. *Sci. Rep.* **2025**, *15*, 1184. <https://doi.org/10.1038/s41598-024-85014-7>.
43. Wang, J.; Guo, X.; Bian, C.; et al. Roadmap for electrochromic smart devices: From materials engineering and architectures design to multifunctional application. *Prog. Mater. Sci.* **2025**, *153*, 101461. <https://doi.org/10.1016/j.pmatsci.2025.101461>.
44. Zhai, Y.; Zhu, Z.; Zhou, S.; et al. Recent advances in spectroelectrochemistry. *Nanoscale* **2018**, *10*, 3089–3111. <https://doi.org/10.1039/c7nr07803j>.
45. Guo, J.; Liang, Y.; Zhang, S.; et al. Recent progress in improving strategies of metal oxide-based electrochromic smart window. *Green Energy Resour.* **2023**, *1*, 100007. <https://doi.org/10.1016/j.gerr.2023.100007>.
46. Wang, Z.; Wang, X.; Cong, S.; et al. Towards full-colour tunability of inorganic electrochromic devices using ultracompact fabry-perot nanocavities. *Nat. Commun.* **2020**, *11*, 302. <https://doi.org/10.1038/s41467-019-14194-y>.
47. Wang, S.M.; Hwang, J.; Kim, E. Polyoxometalates as promising materials for electrochromic devices. *J. Mater. Chem. C* **2019**, *7*, 7828–7850. <https://doi.org/10.1039/c9tc01722d>.
48. Wang, Y.; Shen, G.; Tang, T.; et al. Construction of doped-rare earth (Ce, Eu, Sm, Gd) WO₃ porous nanofilm for superior electrochromic and energy storage windows. *Electrochim. Acta* **2022**, *412*, 140099. <https://doi.org/10.1016/j.electacta.2022.140099>.
49. Dallaev, R. Conductive Polymer Thin Films for Energy Storage and Conversion: Supercapacitors, Batteries, and Solar Cells. *Polymers* **2025**, *17*, 2346. <https://doi.org/10.3390/polym17172346>.
50. Wang, S.; Cai, S.; Cai, W.; et al. Organic-inorganic hybrid electrochromic materials, polysilsesquioxanes containing triarylamine, changing color from colorless to blue. *Sci. Rep.* **2017**, *7*, 14627. <https://doi.org/10.1038/s41598-017-15337-1>.
51. Ahlawat, N.; Bansal, L.; Sahu, B.; et al. A Viologen/ α -MnO₂ Inorganic/Organic Hybrid Assembly-Based Solid-State Electrochromic Device: Improved Performance and Multiwavelength Switching. *ACS Appl. Electron. Mater.* **2025**, *7*, 5712–5720. <https://doi.org/10.1021/acsaem.5c00782>.
52. Wu, Y.; Mishra, Y.K.; Xiong, J. Electrochromic materials: Scope for the cyclic decay mechanisms and performance stability optimisation strategies. *Color. Technol.* **2024**, *140*, 208–229. <https://doi.org/10.1111/cote.12729>.
53. Kong, S.; Li, M.; Xiang, Y.; et al. Machine learning-guided investigation for a high-performance electrochromic device based on ammonium metatungstate-iron(II) chloride-heavy water electrochromic liquid. *J. Mater. Chem. C* **2023**, *11*, 12776–12784. <https://doi.org/10.1039/d3tc02522e>.
54. Shu, Y.; Miao, N.; Li, R.; et al. Machine learning-enabled optoelectronic material discovery: A comprehensive review. *J. Mater. Inform.* **2025**, *5*, 36. <https://doi.org/10.20517/jmi.2025.13>.
55. Zhu, M.; Xu, B.; He, T.; et al. Smart Electrochromic Devices for Wearables. *Adv. Mater. Technol.* **2025**, *10*, e01015. <https://doi.org/10.1002/admt.202501015>.
56. Yu, J.; Wang, S.; Gao, L.; et al. Recent advances in flexible multifunctional electrochromic devices. *Nanoscale* **2025**, *17*, 6919–6937. <https://doi.org/10.1039/d4nr04074k>.
57. Zhang, W.; Liu, G.; Zhang, Z.; et al. Flexographically Printed PEDOT:PSS Electrodes Enabling Stable Paper-Based Self-Powered Electrochromic Devices. *ACS Appl. Polym. Mater.* **2026**, *8*, 2030–2043. <https://doi.org/10.1021/acsapm.5c04031>.