Trends in Electrochromic Materials: Industrial Perspective in Colombia

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ABSTRACT
Dissertations across various sectors (industrial, governmental, and research) advocate for the manufacture of products with innovative scientific and technological developments as a driving force to generate added value and, in a dual approach, respond to the expectations of domestic consumers and encourage exports in the country. This analytical and descriptive bibliometric review on electrochromism, a property of some materials that allows them to reversibly change their optical transmittance via the repeated and consecutive intercalation and extraction of electric charges under a small alternating polarity electric potential, contributes by describing the fundamentals, recent research advances, and the feasibility of national industrial application, given the existence of mineral resources, chemical inputs, companies, and qualified human talent at different levels of sectors related to chromic devices and energy storage.

Keywords: electrochromic devices, eco-energy technologies, resources assessment

Introduction
Between 2000 and 2019, the increase in the per capita gross domestic product (GDP) of Colombia has reached 3.3%, the highest since 2014 (DANE, 2020a). This has not been enough to circumvent structural weaknesses at the international level in terms of technological change. The Colombian economy has a low complexity and is poorly diversified; although the Gini, a measure of a country’s inequality, went from 0.56 in 2010 to 0.476 in 2017 (OECD, 2019), it is still one of the highest in Latin America. In 2019, the monetary poverty gap was 35.7%, and extreme monetary poverty was 9.6% in the national total (DANE, 2020b). Exports based mainly on unprocessed mining and total factor productivity (TFP) generated negligible growth between 2000 and 2019, which is associated with low leverage in research and development (R&D) and industrial interest in technology-based process innovation.

Reflections on improving the GDP converge to the interaction between science, technology, and innovation through the creation of products or services where public or private investment generates added value to the country’s resources, with an important impact on social and environmental challenges (MINICIENCIAS, 2020). The introduction of technologies with chromic properties, in the form of materials with usable characteristics in the country’s glass and mirror industry, could significantly contribute to the assertive engagement of research groups in the technological innovation required by this sector.

Chromic properties include the displacement of the absorption and emission spectra of certain dyes upon application of an electric field, an effect called electrochromism, which can analogously be referred to as thermochromism and photochromism, which describe the...
color changes produced by heat and light, respectively. In particular, an electrochromic material experiences persistent but reversible color change via an electrochemical reaction, as a result of different visible electronic absorption bands between redox states. The color change is caused by a transition of electrons in the region of the molecule (i.e., the chromophore) to a higher energy orbital.

The first report of thin tungsten oxide films as an electrochromic material under potentiostatic or galvanostatic control dates to 1960 (Shi et al., 2020a). This was achieved using three-electrode circuits, electrochemical techniques such as cyclic voltammetry, coulumbimetry, and chronoamperometry, and in situ spectroscopic measurements. In the 1960s, the American Cyanamide Corporation found analogous results for niobium oxide (Bulja, 2017), and electrochromic materials started to attract research interest with a view to develop applied technologies.

Electrochromism was first considered for use in information displays, and, during the first half of the 1970s, several companies such as IBM, Philips, and Canon undertook research efforts (Yang et al., 2016). However, this technology became less important in the 1970s due to the rise of liquid crystal in displays. In 1984, its use was proposed in energy-efficient buildings, and, since then, electrochromism research evidences a powerful momentum. The term smart window came into being between 1984 and 1985 and attracted immediate attention, not only from scientists but also from the media and the general public since smart optical variation can be used in saving energy (Bulja, 2017).

In the last two decades, scientific and technological interest in applications involving electrochromic materials, substrate, and binding electrolytes has been evident, given their potential applications in smart windows and conductive materials in the fields of energy conversion and nanotechnology (Varghese-Hansen et al., 2018). Correspondingly, the question arises whether Colombia would be able to consolidate industries for the manufacture of chromic devices such as smart windows, solar cells, photometric mirrors, and thermochromic or gasochromic glasses, utilizing its mining resources for industrial infrastructure and national scientific agendas.

The analytical review presented herein has two purposes: on the one hand, to present the lines of research from the last five years which have focused on scientific advances regarding electrochromic materials and their components for manufacturing chromic devices; and, on the other hand, to define opportunities for establishing Colombian technology-based companies in this sector.

**Methodology**

Our descriptive and systematic review on electrochromism, including the definition of the concept, its applications, and research gaps, used primary sources (research articles) and secondary sources (review articles and technical reports) published between 2015-2022, which were retrieved from databases such as ScienceDirect, Springer, Taylor & Francis online, Redalyc, Ebsco, and SciELO. Scopus statistics associated with citations and other characteristics (e.g., country of origin) were evaluated. The search strategy considered the following concepts in addition to electrochromism: photochromism, thermochromism, gasochromism, electrochromic material deposition techniques, and electrochromic material types (organic and inorganic). Since 2,634 articles were found, those with the highest number of citations were selected, for a total of 130 documents.

To determine the feasibility of implementing chromic technologies in the country, we analyzed the tertiary information detailed in technical reports and databases of governmental entities, such as the National Administrative Department of Statistics (DANE), the Ministry of Science, Technology, and Innovation (MINCIENCIAS), the Ministry of National Education, the Ministry of Commerce, the Ministry of Mines and Energy, the Geological Service, and the National Mining Agency.

**Results and discussion**

**Smart windows**

An electrochromic device, also called a smart window, is a display unit that allows for electrochemically driven modulations of light transmission and reflections (Li et al., 2019; Kumar et al., 2016; Tsige et al., 2020). The potential market for smart windows is very large and includes rear-view mirrors, sunroofs, and side and smart windows in the automotive sector. Other uses include large-area information displays for use in airports and railroad stations and electrochromic eyeglasses and sunglasses.

In smart windows, the entire system is in the optical path, which imposes some restrictions on the electrolyte used. This electrolyte must be transparent or electrochromic and complementary to the primary electrochromic electrode. These requirements are not easy to meet, and, therefore, most research is devoted to the characterization of materials capable of ensuring the desired switchable complementary optical function. Electrochromic windows can be combined with solar cells, so the energy required for electrochromic color switching can be obtained from them (Yun et al., 2019).

**The physicochemical principle of electrochromism in the manufacture of smart windows**

The reversible change in the optical properties of a material, which is produced by oxidation-reduction induced by electrochemical processes, is called electrochromism (Shi et al., 2020a). This process is exploited in the fabrication of
Electrochromic films can be elaborated using different methods and techniques. Figure 2 consolidates the reports associated with electrochromism and different chromic film deposition methods. Regarding the number of publications, the magnetron sputtering technique far outperforms the others, including sol gel chemical deposition (dip coating) (Wen-Cheun et al., 2019). Other techniques with a smaller number of publications are electrochemical deposition (Kimura et al., 2018), thermal evaporation (El-Nahass et al., 2015), pulsed laser deposition (Farhad, 2021), spray pyrolysis, and spin coating (Paipitak et al., 2011).

Figure 2. Number of publications on different types of chromic material deposition.
Source: Scopus data for “Electrochromism and deposition technique” as of November 2020

Multilayer devices, which consider sandwich structures, consist of inner active ion storage or counter electrode layers, an ion conductive layer (electrolyte), and an electrochromic film (working electrode), utilizing both organic and inorganic substances (Figure 3). Transparent electrode layers are designed while prioritizing a high transparency, low resistance, and easy deposition. Finally, the protective layers use substrates that can be rigid (e.g., glass) or made up of polymers, allowing for flexible systems such as polyethylene terephthalate (TEP).

Figure 3. Electrochromic device with different conductive polymers
Source: Authors

The publications on electrochromism from 1960 to 2020 amount to 8,405, with a steeper slope in the last decade (Figure 4).

Figure 4. Evolution of publications on electrochromism
Source: Scopus data for “Electrochromism” as of November 2020
These figures reveal a more pronounced trend in Eastern countries, where technological application is in constant growth, followed by the United States. Figure 5 shows the countries reporting at least 200 related publications.

The Americas account for 16.84% of the publications. However, excluding the United States, only 473 contributions were considered (Figure 6). The particular case of Colombia exhibits a deficit in associated studies. According to Scopus, only five contributions feature Colombian researchers and three are linked to national universities (Chen P., 2020; Kalay et al., 2020), even though this country has mining resources such as W, Mo, Ni, Ti, and Zn, among others, which could be oriented towards the manufacture of electrochromic devices with technological added value (Zhang et al., 2020).

Electrochromic materials

Electrochromic materials fall into three categories: metal oxide films (De Ribamar-Martins-Neto et al., 2016), molecular dyes (Barile et al., 2017), and conducting polymers (Barus et al., 2018). Electrochromic layers switch their optical properties between their oxidized and reduced forms. In an electrochromic device based on cathodic and anodic layers, applying a voltage to transport ions between the two films in one direction causes both films to become colored, and transporting ions in the opposite direction decolorizes them. Thus, optical modulation and visual appearance can be extended by optimizing both electrochromic layers.

Table 1 exemplifies some electrochromic materials and their potential technological use: transition metal oxides, widely used in smart windows, thermochromics, satellite systems, and chemical paper; Prussian blue systems and metallic phthalocyanines that allow for different color ranges, which are used in monitors; viologen compounds, with applications in smart windows and smart mirrors (such as rear-view mirrors); and conductive polymers, which, in addition to mobile devices, are used in solar cells, artificial muscles, and smart windows.

<table>
<thead>
<tr>
<th>Electrochromic material</th>
<th>Examples</th>
<th>Applications</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition metals (oxides)</td>
<td>WO₃, MoO₃, V₂O₅, Nb₂O₅, Ir(OH)₃, and NiOₓHₙ</td>
<td>Intelligent windows, thermal satellite control</td>
<td>(Richardson, et al., 2018)</td>
</tr>
<tr>
<td>Prussian blue systems (PB)</td>
<td>Prussian blue, Prussian brown, Prussian green, and Prussian white</td>
<td>Monitors</td>
<td>(Pan, 2020)</td>
</tr>
<tr>
<td>Viologens</td>
<td>Salts of 1,1'-disubstituted 4,4'-bipyridine</td>
<td>Mirrors, monitors</td>
<td>(Zeng, 2021)</td>
</tr>
<tr>
<td>Conductive polymers</td>
<td>Poly(3,4-ethylenedioxythiophene), polypyrrole, polythiophene, Poly(styrene sulfonate)</td>
<td>Intelligent window and screens</td>
<td>(Wang L., 2020),</td>
</tr>
<tr>
<td>Metallic phthalocyanines</td>
<td>[Lu(Pc)₃] (C₂H₄N₄)</td>
<td>Monitors</td>
<td>(Ho et al., 2015)</td>
</tr>
</tbody>
</table>

**Source:** Authors

**Metal oxides**

Transition metal oxide films, e.g., iridium (Sun, 2015; Jang and Lee, 2020), rhodium (Jeong, 2020), ruthenium (Wang Y. et al., 2019), tungsten (Atak et al., 2020; Pan, 2020), molybdenum (Hasani, 2017), possess electrochromic properties, with tungsten oxide and molybdenum oxide being the most widely studied. This type of electrochromic material can be classified into inorganic electrochromic materials that can be deposited through vacuum evaporation (Sahu et al., 2017; Gupta et al., 2022b), sputtering (Murphy et al., 2016; Kumar et al., 2022; Kumar et al., 2022a; Kumar et al., 2022b), electrodeposition (Dulgerbaki et al., 2018), tungsten metal electrochemical oxidation (Lin, 2020), and the sol-gel method (Zhang et al., 2019), among others. Metal oxide films can be electrochemically modulated to a non-stoichiometric redox state, which has an intense electrochromic absorption band due to optical range charge transfer.

Transition metal oxides with electrochromic properties can be colored cathodically or anodically, depending on the
material that is colored under ion injection or extraction, i.e., via a reduction or oxidation (Besnardiere, 2019). Cathodic coloration (blue) has been reported for Ti, Nb, Mo, Ta, and W oxides, with tungsten oxide (WO₃) being the first and most widely studied. Anodic coloration (red) is associated with Cr, Mn, Fe, Co, Ni, Rh, and Ir oxides, with nickel oxide (NiO) and iridium oxide (IrO) being the most reported (Wang Z. et al., 2020; Ding, 2021).

Table 2 presents some examples of coloration changes in both oxidized and reduced states, as well as the applied potential range of cathodic and anodic ionic insertion materials that are colored through electrochemical oxidation. The studies are aimed at obtaining the highest contrast between the oxidized and reduced state, as well as shades in the entire color range.

For cathodic oxides, the color variation can be established at any absorption level between states with maximum and minimum absorption. The mechanisms for optical absorption are still scarcely understood. However, they generally associated with charge transfer and polaron absorption (Sun, 2020; Szkoda et al., 2020; Rathika, 2020).

Table 2. Electrochromic characteristics of some metal oxides

<table>
<thead>
<tr>
<th>Cathode, c Anode, a</th>
<th>Oxidized state</th>
<th>Reduced state</th>
<th>E (V)</th>
<th>Area</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₃ c NiO</td>
<td>Transparent</td>
<td>Blue</td>
<td>0,5</td>
<td>2,5 cm²</td>
<td>(Szkoda et al., 2020)</td>
</tr>
<tr>
<td>V₂O₅ c</td>
<td>Yellow</td>
<td>Black, blue</td>
<td>0,2</td>
<td>1,5 cm²</td>
<td>(Rathika, 2020)</td>
</tr>
<tr>
<td>WO₃ c NiO</td>
<td>Transparent</td>
<td>Blue</td>
<td>0,4</td>
<td>4 cm²</td>
<td>(Bayrak et al., 2021)</td>
</tr>
<tr>
<td>Ir(OH)₃ a Ni(OH)₂ a</td>
<td>Blue black</td>
<td>Transparent</td>
<td>0,5</td>
<td>2,5 cm²</td>
<td>(Jiang et al., 2008)</td>
</tr>
<tr>
<td>Ni(OH)₂ a</td>
<td>Maroon</td>
<td>Transparent pale green</td>
<td>0,2</td>
<td>3 cm²</td>
<td>(Morales-Torres et al., 2009)</td>
</tr>
</tbody>
</table>

Source: Authors

For example, WO₃ exhibits a highly efficient blue coloration in amorphous films, which can reversibly change from transparent to dark blue by electrochemical redox reactions (Jittiarporn et al., 2017; Gupta et al., 2021; Gupta et al., 2022a). Coloration characteristics depend on the constitution and composition of the film, as well as on the atomic structure and size of the nanoparticles, pores, and adsorbed substances. The insertion/extraction process can be represented via the following Equations:

\[ WO₃ + x \left( M⁺ + e⁻ \right) (\text{Transp.}) M_xWO₃ (\text{Blue}) \quad (1) \]

\[ WO₃ + x \left( Li⁺ + e⁻ \right) (\text{Transp.}) Li_xWO₃-W_{x}^{4+}WO_{y}^{5⁻} (\text{Blue}) \quad (2) \]

Tungsten trioxide, with all tungsten atoms in a W⁴⁺ oxidation state, is a transparent thin film. During electrochemical reduction, W⁵⁺ sites are generated to provide the electrochromic effect. The applications of electrochromism include manufacturing solid-state devices, where Li⁺ is most often used. Applications have also been reported with Al³⁺ ions, given their affinity with tungsten trioxide (Li W., 2020; Tang et al., 2020; Yao, 2020; Kumar et al., 2022b).

The properties of WO₃ are combined with other electrochromic materials such as Nb₂O₅ (Tang, 2019), conductive polymers (Brooke et al., 2018), and viologens (Yu, 2020) to improve contrast and color change efficiency. In commercial applications, as is the case of prototype alphanumeric displays, electrochromic mirrors are employed (Kim, 2016).

Although the W⁴⁺/W⁵⁺ interval transition model mentioned above is the most accepted theory, which implies electron delocalization and is consistent with the conductivity enhancement that accompanies the insertion processes (Gesheva, 2016), other models involving non-localized electrons or bond interaction (Meenakshi et al., 2016) have been proposed to explain the electrochromic mechanism of tungsten oxide and inorganic ion insertion compounds in general.

The characteristics of the electrochromic process can be conventionally examined by directly comparing the optical and electrochemical response of the WO₃ electrode. The cyclic voltammetry and optical transmittance of a WO₃ electrode has been measured in a cell with a Li⁺ ion-conducting electrolyte and a counter electrode (Dong, 2018).

Among the anodic oxides, nickel oxides with Li⁺ electrolytes have been comprehensively studied. Nickel oxide can be bleached or colored by moving the Fermi level near the top of the valence band up or down. The electrochemical cycling of nickel oxide in different electrolytes takes place through the exchange of H⁺ and OH⁻. Given the nature of the film and the electrolyte, as well as the coloration mechanism of NiO, this is regarded as a surface phenomenon (Dong, 2020). After ion insertion and removal, the lattice constant of NiO exhibits changes in the grain unit cells (Kalanur et al., 2020). The coloration of nickel oxide is based on the transition between Ni²⁺ and Ni³⁺ (Morales-Torres et al., 2009)

\[ NiOH₂ + \text{Bleaching} \quad NiOOH (\text{colored}) + H⁺ + e⁻ \quad (3) \]

Electrochromism has been studied under two possible cycling modes: the response between coloration and bleaching in steps of increasing potential (shift) and stepwise modulation towards coloration with increasing power and back to bleaching (modulation), observing that NiO films during oxidation exhibit a change in coloration.
Electrochromism and energy exchange functions can be achieved through redox reactions, indicating that the design of a bifunctional electrochromic energy storage device is feasible. In this context, NiO has been studied regarding its stability and compatibility with WO₃ electrodes (Firat and Peksoz, 2019; Huang et al., 2018). Likewise, the addition of surfactants such as dodecyl sulfate entails changes in the microstructure, morphology, and electrochromic performance of NiO films (Pham et al., 2020).

The hybrid cell design of WO₃ and NiO films obtained by sputtering reports a coloration efficiency of 360 cm²C⁻¹ at 640 nm, which depends on sputtering conditions (Koo et al., 2020). The hexagonal electrode assembly of WO₃ and NiO nanoparticles allows obtaining optical modulation values of 67.6% at 630 nm, a coloration efficiency of 109.6 cm²C⁻¹, fast switching speeds (7.9 s), and a cycle life with a remaining ΔT of 84.1% after 4 000 cycles (Thumnavichai et al., 2017).

Another important factor affecting the electrochromic performance of NiO films is thickness; the optical transmission of the films decreases as their thickness increases. X-ray diffraction patterns reveal that polycrystalline phase and peak density increase with film thickness. The optical forbidden band decreases by about 0.2 eV with increasing film thickness, with values of 480 nm boasting a good performance (Atak and Coşkun, 2019). NiO nanocomposite films with gold for supercapacitor applications exhibit greatly enhanced pseudo-capacitive properties, 1.5 times higher than those of pure NiO (Jung, 2020).

Reports show more interest in NiO electrochromophores at the counter electrode, i.e., as a redox reagent at the second electrode of an electrochromic cell. Here, there is a reactive primary electrochrome, such as WO₃ (Zheng, 2018) and conductive polymers such as poly(pyrrole), poly(thiophene), and poly(methylthiophene) (Liu Z., 2019). When it comes to the coloring mechanism, it should be noted that cathodic oxide (WO₃) and anodic oxide (NiO) films are different regarding their electrochemical performance. Ions can enter the lattice structure of cathodic oxide, whereas, in a Li⁺-containing electrolyte, surface electrochromic processes dominate NiO films.

**Viologens**

The term viologen was coined by Michaelis and Hills for 4,4r-dipyridium compounds because they turn deep blue purple upon reduction. The ion may exhibit a two-step reduction, i.e., one electron, or a two-state reduction (Monk et al., 2015).

The most widely studied material in the viologen family is methyl viologen (MV). Elofson and Edsberg reported the first electron reduction of MV at 0.6 V vs. ECS. The coplanarity of the two heterocyclic nuclei facilitates a pH-independent, reversible reduction. The second electron reduction is not electrochemically reversible, but MV can be reoxidized by air. Reports state that the second reduction at 1.038 V vs. ECS is independent between 5.0 and 13.0 pH units and slightly dependent at a pH below 5.0 (Gugole, 2020).

Electrodes can be functionalized with electrochemically active polymeric materials derived from the hydrolytically unstable viologen, N, N'-bis [-3-(trimethoxysilyl) propyl]-4,4r-bipyridinium dibromide, which shows potential for improved electrochromic efficiency in solid-state devices. Conventionally, electrochromic displays achieve contrast change by modulating light via the optical absorption of the electrodeposited film (Gugole, 2020).

The color change experienced by viologens is related to the functioning of the nitrogen substituent. For example, if the substituent is n-heptyl, a purple deposit is obtained; if it is p-cyano-phenyl, a green deposit is obtained. In addition, the electrical properties of the deposit can be tailored via the selection of the anion. Thus, for viologens of n-heptyl and bromide anions, the deposit is conductive, whereas the substitution of bromide with dihydrogen phosphate anions generates precipitates with insulating characteristics (Mishra, 2017). It has been reported that electrochromic devices based on viologens exhibit reversible multicolor changes at low voltages, with optical contrast values reaching 62.5% between 617 and 716 nm (Xu Z., 2020).

**Conductive polymers**

Conductive polymers have a leading role in the current challenges associated with efficient energy production. An example of this is their applications in fuel cells, with benefits for the economy and the versatility of shape and weight. Electrocactive polymers show potential in technological applications such as electrodes in batteries (Wang L., 2020), microelectronics (Li S., 2020), electrochromic...
materials for sensor devices (Tsai et al., 2021), and catalyst support in fuel cells (Liu et al., 2019), among others. Conventionally, electrochromic displays achieve contrast change by modulating light via the optical absorption of the electrodeposited film, and they are good ionic and electronic conductors, with low processing costs and weight when compared to metallic materials used as electrodes.

Resistance to corrosive conditions in the cell and a porosity that enables permeability to ions (e.g., hydrogen ions) significantly increase the reaction area. The lower thickness in comparison with metal oxides facilitates the serial assembly of several cells in reduced sizes, which has made electroactive polymers the most widely applied materials in fuel cells (Pandey, 2016). These are electrochromic materials that offer a high degree of color matching by coupling various polymer systems through functionalization and/or copolymerization of monomers, as well as through the use of blends, laminates, and composites. Complex colors are achieved by mixing two existing colors in a dual-polymer device. Electrochromic changes are induced by redox processes accompanied by ion insertion/expulsion, and the color exhibited by the polymer is closely related to the band gap and the doping ions. A focus area in the study of electrochromic polymeric materials is the control of their colors by modifying the structure of the main and pendant chain group. Polyheterocycles have proven to be of special interest in this regard due to their stability under ambient conditions (Matysiak et al., 2020). Table 3 provides a comparison of the electrochromic properties observed in the most widely studied conductive polymers.

Table 3. Electrochromic effect of some conductive polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Anion</th>
<th>Oxidized state</th>
<th>Reduced state</th>
<th>Time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy</td>
<td>ClO₄⁻</td>
<td>Brown</td>
<td>Yellow</td>
<td>20</td>
</tr>
<tr>
<td>Polythiophene</td>
<td>ClO₄⁻</td>
<td>Brown</td>
<td>Green</td>
<td>45</td>
</tr>
<tr>
<td>Polymethylthiophene</td>
<td>BF₄⁻</td>
<td>Blue</td>
<td>Red</td>
<td>12</td>
</tr>
<tr>
<td>PEDOT</td>
<td>ClO₄⁻</td>
<td>Dark Blue</td>
<td>Blue</td>
<td>60</td>
</tr>
<tr>
<td>Poly-2,2r-bithiophene</td>
<td>SF₆⁻, SO₄⁻</td>
<td>Blue</td>
<td>Red</td>
<td>40</td>
</tr>
<tr>
<td>Octacyano phtha-locyanine</td>
<td>H⁺</td>
<td>Grey</td>
<td>Green</td>
<td>1</td>
</tr>
<tr>
<td>PANI</td>
<td>Cl⁻</td>
<td>Blue-green</td>
<td>Yellow</td>
<td>100</td>
</tr>
</tbody>
</table>

Source: Authors

Polypyrrole (PPy). The first PPy films were usually prepared via the electrochemical polymerization of pyrrole (Py) in an aqueous or organic solvent solution such as acetonitrile, together with a suitable electrolyte. This process involves the oxidation and dimerization of Py (Yin, 2020). The polymerization reaction involves two electrons per reacting Py molecule, and the resulting polymer is produced in an oxidized state with 0,25-0,33 cation centers per unit of Py depending on the electrolyte (Matysiak et al., 2020). The doped (oxidized) PPy film is blue-violet (λ max 670 nm), and electrochemical reduction produces an ‘undoped’ yellow-green form (λ max 420 nm) (Kazazi, 2019). PPy and polyindole (PIn)-based electrodes exhibit a high degree of flexibility, which makes them remarkably suitable and applicable for fabricating flexible supercapacitors. Py derivatives with methyl red (PMRPy) electropolymerized on glass electrodes improve chromatic contrast (Δ%T=34,2%), switching times (τ=10 s), and stability (Δ%T=15% in the 100th cycle) with respect to Ppy films. Their coloration changes (magenta in acidic media and yellow in basic ones) can be used in pH sensors (Choudhary et al., 2020).

Polythiophene. The electrochromic properties of polythiophene and polymers of various substituted thiophenes are a matter of great interest, as color states can be tuned via the appropriate choice of thiophene monomer. For example, the electrochromic properties of polymer films prepared with 3-methylthiophene-based oligomers strongly depend on the relative positions of the methyl groups in the polymer’s main chain (Table 4), and multicolor systems can be constructed by combining different conducting polymer species. Polypyrrole (PEDOT) can prevent halogen ion poisoning in the reactive area in protic media (Dias et al., 2019). PPy thin films can be prepared via the electrochemical polymerization of 3,4-ethylenedioxythiophene. During the electropolymerization process, the anion in the electrolyte directly influences the uniformity, morphology, and electrochromic performance of PEDOT films (Xu D., 2020).

Table 4. Most common polytyophenes and their coloration

<table>
<thead>
<tr>
<th>Monophenols</th>
<th>Oxidized state</th>
<th>Reduced state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiophene</td>
<td>Blue</td>
<td>Red</td>
</tr>
<tr>
<td>3-methylthiophene</td>
<td>Dark blue</td>
<td>Red</td>
</tr>
<tr>
<td>3,4-dimethylthiophene</td>
<td>Dark blue</td>
<td>Pale brown</td>
</tr>
<tr>
<td>2,2r-Bithiophene</td>
<td>Blue-gray</td>
<td>Orange</td>
</tr>
</tbody>
</table>

Source: Zhang and Feng (2020)

Electrochromic layers of PEDOT copolymerized with polystyrene sulfonate (PSS) and intercalated on a Ni lattice (Chen, C. 2020), Au/PEDOT/Pt microtubes on WO₃ films (Karaca et al., 2019), the imidazole/Fe(III) p-toluensulfonate weight ratio (Wang W., 2020), the adhesion to acidified nanostructured tubular nanostructured silicoaluminate clays, and Halloysite (HNT) (Hu et al., 2019) allow obtaining devices with short staining and decolorization times (less than 20 s), high optical contrast (close to 90%), staining efficiency (higher than 300 cm²C⁻¹), and excellent mechanical
reliability, which corresponds to optical contrast retention after 1,000 cycles (Zhang and Feng, 2020).

**Polyaniline (PANI).** The electrical and electrochromic properties of PANI depend on its oxidation state, its protonation state, the pH of the electrolyte used, the redox mechanisms involving protonation/deprotonation, and/or the input/output of anions, which allows it to exhibit reversible color changes at the potential: transparent leukoesmeraldine to yellowish green emeraldine to dark blue-black pernigraniline in the potential range of -0.2 to +1.0 V vs. SCE (Begum et al., 2013).

The use of donor-acceptor systems between PANI films and porous structures between them facilitates the diffusion of the ions involved in charge transfer reactions, exhibiting increased device performance, contrast parameters close to 38.5%, redox reaction efficiencies close to 200 cm²C⁻¹, response speeds close to 1.0 s, and cyclic stability, with optical modulations of 98% for at least 5,000 cycles.

Some examples of multifunctional electrochromic devices that also exhibit energy storage capabilities and are based on organic/inorganic composites include the insertion of Cu(III) ions in PANI films (Deshmukh et al., 2017), nanostructured mesoporous Ni-PANI thin film electrodes (Inamdar et al., 2019), nanofibers of PANI entrapped in antimony-doped tin oxide, nanofilaments using aminophenyl diazonium cations as precursors of semiconducting mesoporous Ni-PANI thin film electrodes (Inamdar et al., 2019), nanofibers of PANI entrapped in antimony-doped tin oxide, nanofilaments using aminophenyl diazonium cations as precursors of polydiphenylamine and monodisperse PANI via oxidative polymerization of aniline monomers (Jamdegni and Kaur, 2020), W₆O₁₉/PANI hybrid films (Chang, 2018), and V₂O₅/PANI composites obtained through in situ chemical oxidation polymerization (Zhang, 2018).

The versatility of polymers allows for couplings of different families, self-assemblies (e.g., polystyrene and PANI films using natural sedimentation and in situ polymerization of aniline monomers) (Wu, 2019), thin core/film structure formation through π-π stacking between aromatic rings of polydiphenylamine and monodisperse PANI via oxidative polymerization (Han et al., 2020), and semiconductorized polymeric polygalic acid (PGA) templates with PEDOT and PANI in complexes that can be processed by sputter coating to produce flexible electrochromic devices (Díaz-Sánchez et al., 2019), among others, improving features such as the efficiency, contrast, and permutation cycles of smart windows.

The color change and conductivity of PANI films are applied in the design of other types of devices, such as multicolor immunoassay platforms for clinical diagnostics. With visible light excitation, Ag,S NPs@ZnO NPs generate electron holes. The photoelectrons pass into the PB and the photoinduced holes oxidize the PANI, causing color change from emerald green to purple-blue and black depending on the carcinoembryonic antigen’s concentration (Wang Y. et al., 2020). Conductive emulsions of PANI and polyacrylate (PA) obtained via chemical polymerization in the presence of poly (maleic anhydride-co-co-acrylic acid-co-sodium p-styrenesulfonate) as a stabilizer exhibit the electrical conductivity and mechanical properties necessary for applications in antistatic fabric finishing and functional textile development (Wu L. et al., 2018). Likewise, the structural stabilization of PANI films obtained by coating conductive carbon nanotube networks provides multiple directions for electron transfer and, therefore, improves charge capacity by forming 3D networks and enhancing optical transmittance and capacity, which is relevant in the construction of smart supercapacitors (Xu K., 2020).

**Electrolytes**

In electrochromic devices, when a potential is applied, the ions in the electrolyte are transported between the layers, generating a change in the transparency of the chromic material. The initial electrolyte prototypes had aqueous characteristics, entailing conductivities that were nowhere near the expected values (around 1 mS.cm⁻¹) for industrial applications, which demand reliable, safe, and easily transportable and implementable architectures. Hence, there is a global search for electrolytes that allow manufacturing solid-state electrochromic devices.

Lithium-based electrolytes have gained great attention due to their environmental stability. They are made up of mixtures of LiClO₄ and one or more polymers such as polyvinyl chloride (PVC) (Hernández, 2020), propylene carbonate (PC) and ethylene carbonate (EC) (Dalavi et al., 2020), and aprotic salt with polymethylmethacrylate (PMMA) (Ganesh et al., 2015), which entails a transmittance higher than 90% and a durability greater than 5,000 cycles. However, there are other types of electrolytes, e.g., ionic liquids such as coPIL, which is composed of trioxethylen and tetroxyethylen spacers containing 1,2,3-triazolium and offers high degradation temperatures (230 °C) and an ionic conductivity lower than 9×10⁻⁵ Scm⁻¹. This has allowed for conversion times shorter than 12 s and stability after 3,000 cycles (Puguan and Kim, 2019). Gelatin-based solid electrolytes, cross-linked with formaldehyde, glycerol, acetic acid, and/or HCl have also been used, obtaining ionic conductivity values of 1,28×10⁻⁵ Scm⁻¹ and a percent transmittance of 98% at wavelengths above 580 nm (Ramadan et al., 2017). Environmentally friendly hydrogels containing deionized water, sodium carboxymethylchitosan, and vitamin C are used as electrolytes of the electrochromophore bis (2-(2-(2-hydroxyethoxy) ethoxy) ethyl) viologen bromide, with colorless to purple shifts between 0 and -1.2 V (Zhang Y. et al., 2021), among others. Some authors integrate ITO/VO₂/LiTaO₃/WO₃/ITO-type devices on glass substrates, where several chromic processes are evidenced: a thermochromic layer passively responding to ambient temperature, another electrochromic layer actively and simultaneously responding to external voltage, and reversible Li⁺ migration within the lattice at low bias voltages (Jia, 2019).
Table 5 compiles some focus points regarding potential electrochromic devices for use in smart windows.

**Possibilities for chromic materials innovation in the Colombian industry**

Colombia exhibits a significant extraction of Fe, Co, Ni, Mo, C, W, and Ti, mainly in the northern part of the country, Cundinamarca, and the coffee axis region, which would allow consolidating industrial applications with tungsten and nickel oxide inputs. There are also tungsten deposits in the departments of Guaviare, Vichada, and Caquetá, where extraction activities were carried out between 2012 and 2016. Although the country lacks information on the extraction or production of tungsten as a mineral, information from DANE allows stating that the national industries’ consumption is centered on tungsten plates. Imports of tungsten come in the form of sintered bars (industrial materials composed of tungsten) and not in the mineral’s raw form. On the other hand, the country showed exports of 87 metric tons between 2012 and 2015 (Prieto et al., 2019). Likewise, in Colombia, there are six nickel deposits, three of which are in the Caribbean region, i.e., in the department of Córdoba: Cerro Matoso, Planeta Rica, and Uré. The remaining three are in the department of Antioquia: Ituango, Morro Pelón, and Medellín. Colombian nickel production remains above 40,000 tons since 2012 (DNP, 2017). Data as of 2018 establish Colombia as the first producer of nickel in South America and the third in Central America and the Caribbean, only after Cuba and the Dominican Republic (MINMINAS, 2018).

A strategic union between academia and national companies could be the link that the national glass industry needs to become a beacon of electrochromic, gasochromic, or thermochromic technologies. Colombia has industries in the manufacture of flat glass whose inputs are national, such as Tecnoglass SA, Cristar SAS, Cristalería Peldar SA, AGP de Colombia SA, and Fiberglass Colombia SA, among others. The import of raw materials does not exceed 16%, and, regarding mirrors and fibers, it does not reach 19%. Plates and smooth sheets of cast or laminated, unassembled, colored, opacified, and plated glass, as well as glass with absorbent, reflective, or anti-reflective coating, are the most traded products abroad. The United States accounts for 60.25% of the exports, followed by Mexico with 7.76%, Ecuador with 7.65%, and Peru 7.15% (Legis-Comex, 2017).

The manufacture of chemical products in Colombia, which has all the necessary inputs to produce chromic technologies, grew with a compound annual rate of 8.5% between 2000 and 2018. The departments with the highest production of chemical products are Cundinamarca, Antioquia, Valle, and Bolívar. Between 2014 and 2016, the gross production of this sector increased by 21.1%. However, 8.4% of their production facilities closed. Projections for 2030 show a compound annual growth rate of 6.5%, with a market growth rate higher in proportion than that of production (4.7% by 2032) (MINCIT, 2019a). The expectations regarding innovation programs and the strengthening of the chemical supply chain, which include chromic devices, should provide added value, allowing the Colombian chemical industry to replace current imports (MINCIT, 2019b).

Industrial-level scientific initiatives on topics related to smart windows and mirrors can be covered by the lines of research that MINCIENCIAS has been promoting, which focus on converging technologies and the Industry 4.0, especially on nanotechnology, competitiveness, and productivity; sustainable energy, aiming for energy efficiency in heating systems, lighting in urban areas, direct and indirect heat, and/or efficient energy management; and geosciences, promoting the identification, characterization, quantification, and industrial exploitation of mineral deposits with added value (MINCIENCIAS and Vicepresidencia de la República de Colombia, 2020).

The qualified human resources for the implementation and research of chromic devices or related technologies and materials can be supported by more than 50 research groups endorsed by MINCIENCIAS in the 2021 call for proposals (MINCIENCIAS, 2022). In addition, the higher education system has more than 180 professional technical and technological programs, technological specializations, and professional technical specializations, as well as more than 140 professional programs and more than 170 postgraduate programs in areas such as nanotechnology, materials, geology, electronics, clean technologies, energy resources, automation of industrial processes, mines, and chemistry, among others (SNIES, 2021). These programs can be oriented towards theoretical and experimental competencies in innovation in the implementation of industries associated with electrochromic, photochromic, and gasochromic technological devices, in addition to fuel cells, smart windows, and mirrors, among others.

Finally, as for the feasibility of implementing industries that apply chromic properties, the differential capabilities of the Colombian industry should be highlighted. The availability of natural resources; the country’s location; free trade agreements with consumer and producer countries; the culture of cost reduction, quality, and compliance with requirements, regulations, and standards; the institutions that promote the culture of continuous improvement to the production process (Colombia Productiva, INNPulsa and Pro-Colombia); and customer service levels are all factors to be leveraged by companies. However, there is a need to streamline government processes, to train personnel in export policies, to promote internalization in productive clusters that project the acquisition of investors, to support new regulations, and to establish productive linkages in the chemical sector through dialogues aimed at collective development.
Table 5. Electrochromic effect of some conductive polymers

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Electrochromic material deposition method</th>
<th>η (cm²C⁻¹)</th>
<th>∆T (%)</th>
<th>modulation potentials (V)</th>
<th>λ (nm)</th>
<th>Response time (s)</th>
<th>Cycles with retention &gt;90% ∆T</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass/ITO/ WO₃/ LiClO₄ in PC/WO₃⁻⁻, in/ITO/Glass</td>
<td>Cathodic sputtering</td>
<td>1.5 to 4.0, vs. Li⁺/Li⁻</td>
<td>1,5</td>
<td>700</td>
<td>15</td>
<td>500</td>
<td>(Shi et al., 2020a)</td>
<td></td>
</tr>
<tr>
<td>Si/SiO₂/ WO₃/ LiNbO₃/NiO/C</td>
<td>Electron beam evaporation</td>
<td>0.7 to -0.9</td>
<td>0.7</td>
<td>700</td>
<td>15</td>
<td>500</td>
<td>(Buljam, 2017)</td>
<td></td>
</tr>
<tr>
<td>PET/ITO/ WO₃, LiClO₄ in PMMA/ITO/PET</td>
<td>Spin-coating</td>
<td>57.4</td>
<td>85</td>
<td>-0.9 to 0.0</td>
<td>(tb) 15, (tc) 5</td>
<td>1 000</td>
<td>(Yun et al., 2019)</td>
<td></td>
</tr>
<tr>
<td>PET/ITO/ WO₃, LiClO₄ in PMMA/ITO/PET</td>
<td>DC magnetron sputtering</td>
<td>64</td>
<td>-4 to +3</td>
<td>633</td>
<td>(tb) 3.75, (tc) 2.35</td>
<td>5 000</td>
<td>(Chen X., 2020)</td>
<td></td>
</tr>
<tr>
<td>Glass/ITO/ nanopolymers of WO₃/ [C₃mpyr][BF₄]/ITO/Glass</td>
<td>Ultrasonic irradiation</td>
<td>52.4</td>
<td>70</td>
<td>-1.0 to -0.5</td>
<td>520</td>
<td>(tb) 23, (tc) 2.8</td>
<td>500</td>
<td>(De Ribamar Martins Neto et al., 2016)</td>
</tr>
<tr>
<td>Glass/ITO/ Cu-Pb gel in hydroxyethylcellulose/Cu-Ag</td>
<td>Electrodeposition</td>
<td>90</td>
<td>-0.6 to 0.8</td>
<td>600</td>
<td>10</td>
<td>5 000</td>
<td>(Barile et al., 2017)</td>
<td></td>
</tr>
<tr>
<td>Glass/FTO/ TiO₂ (TiPOT)/ ge of citric acid, ethanol, Li₂CO₃, and tetraethyloxyhydrosilicate/FTO/Glass</td>
<td>Spin-coating</td>
<td>82.7</td>
<td>28</td>
<td>-0.6 to -1.8</td>
<td>390 to 2</td>
<td>17,8</td>
<td>400</td>
<td>(Zhang, et al., 2019)</td>
</tr>
<tr>
<td>Glass/FTO/ h”H WO₃/ HSO₄ 0.1M/ Cu</td>
<td>Spin-coating</td>
<td>53</td>
<td>24</td>
<td>±0.8 vs. Ag/AgCl</td>
<td>700</td>
<td>13</td>
<td>150</td>
<td>(Besnardiere, 2019)</td>
</tr>
<tr>
<td>Glass/ITO/ NiO: (Li, Mg)/Ta₂O₅/1 M PC/LiClO₄/WO₃/ITO</td>
<td>DC magnetron sputtering</td>
<td>60</td>
<td>66</td>
<td>±1.5</td>
<td>500 to 600</td>
<td>(tb) 1.0, (tc) 2.5</td>
<td>1 500</td>
<td>(Chen P., et al., 2020)</td>
</tr>
<tr>
<td>Glass/ITO/ WO₃/LiClO₄ PC/ NiO/ITO/ Glass</td>
<td>Cathodic arc plasma</td>
<td>90</td>
<td>46</td>
<td>0.8 to -1.4</td>
<td>633</td>
<td>3</td>
<td>2 500</td>
<td>(Chen P., et al., 2020)</td>
</tr>
<tr>
<td>Glass/ITO/EDBT; EDOT; thiene [3,4-b] pyrazine and benzo [1,2,3] triazole/PEDBT and PMTTP/ITO/Glass</td>
<td>Electropolymerization</td>
<td>64</td>
<td>-0.2 to 1.0</td>
<td>590</td>
<td>1 500</td>
<td>2</td>
<td>(Xu Z., 2020)</td>
<td></td>
</tr>
<tr>
<td>Glass/ITO/PEDOT/KCl 3M, 0.1LiClO₄/Pt</td>
<td>Electropolymerization</td>
<td>15</td>
<td>±3</td>
<td>500-645</td>
<td>(tb) 0.15, (tc) 2.30</td>
<td>2 000</td>
<td>(Xu D., 2020)</td>
<td></td>
</tr>
<tr>
<td>Glass/ITO/Ni mesh / PEDOT:PSS/ TABPF₆/Ni mesh /ITO/Glass</td>
<td>Spin-coating</td>
<td>15</td>
<td>3.5 to -2.5</td>
<td>644</td>
<td>1</td>
<td>1 000</td>
<td>(Chen C., 2020)</td>
<td></td>
</tr>
<tr>
<td>PET/ITO/ WO₃-Au/PEDOT/Pt/ LiClO₄ in PMMA, PC/ITO/PET</td>
<td>Electron beam evaporation: WO₃ Spin-coating: Au/ PEDOT/Pt</td>
<td>26</td>
<td>±2</td>
<td>750</td>
<td>(tb) 13.83, (tc) 19.25</td>
<td>1 000</td>
<td>(Karaca et al., 2019)</td>
<td></td>
</tr>
<tr>
<td>Glass/FTO/PEDOT in (Im/Fe)/ LiClO₄ / FTO/Glass</td>
<td>Vapor phase polymerization</td>
<td>18.5</td>
<td>0.4 to -0.2</td>
<td>550</td>
<td>10</td>
<td>1 500</td>
<td>(Wang, W., 2020)</td>
<td></td>
</tr>
<tr>
<td>Glass/ITO/HNT@PEDOT/0.1 M LiClO₄/ DMSO/ITO/Glass</td>
<td>Oxidative chemical polymerization (HNT) Spin-coating (PEDOT)</td>
<td>174.3</td>
<td>59.3</td>
<td>-0.5 to 0.7</td>
<td>450 to 700</td>
<td>(tb) 2.8, (tc) 2.7</td>
<td>(Hu et al., 2019)</td>
<td></td>
</tr>
<tr>
<td>Glass/ITO/(CuII)/PANI, H₂SO₄ 0.2M/ ITO/Glass</td>
<td>Electrodeposition</td>
<td>10</td>
<td>-0.1 to 1.4</td>
<td>400-900</td>
<td>1.85</td>
<td>(Deshmukh et al., 2017)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

Studies on the physical and chemical properties of diverse organic and inorganic electrochromic materials show potential for the manufacture of electrochromic devices with industrial applications such as rear-view mirrors in the automotive sector, alphanumeric screens, monitors, and intelligent windows, among others. Among the inorganic materials used, NiO (anodic oxide) and WO₃ (cathodic oxide) stand out, which could be regarded as classical electrochromic materials since they boast a better electrochromic performance. Couplings have been made for them with organic materials such as conductive and viologen polymers in the construction of solid-state devices. In addition to electrochromic properties, studies on electrochromic devices have shown a tendency towards the modulation of radiation in the near-infrared, thermal-infrared, and microwave regions. ‘Color’ may represent the detectors’ response to these wavelengths (i.e., thermochromic, photochromic) as well as energy storage capacity in the manufacture of supercapacitors. Widespread applications of architectural electrochromic devices rely on reducing costs, increasing the useful life of the device, and overcoming the issue of degradation. Thus, the use of polymer electrolytes with lithium ions has been widely studied, as well as innovations with ionic liquids and polymers with a low environmental impact.

The trajectory of the Colombian industrial sector, together with the human talent in local research groups, and the training offer for personnel at all levels (technical, professional, and postgraduate) are inputs for the potential implementation of an industry with great social and economic impact. Colombia has mining resources and companies in the glass sector and in the manufacture of chemical products that, if directed towards industrial innovation clusters and leveraged by different sectors of the government and national and international investors, could entail the establishing of companies with

Source: Authors
chromic applications in the medium term, especially regarding the use of inorganic inputs. In the long term, if the country’s chemical industry, which works with petroleum derivatives, shows interest in obtaining inputs related to conductive polymer monomers and viologens applicable in chromic devices, the need to project the manufacture of organic and inorganic chromic materials could be resolved.

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cRediT author statement

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Conflicts of interest

The authors declare no conflicts of interest.

References


