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Introduction

1.1 Electrochromism: A Brief Note on the History and Recent Evolution

Electrochromism can be defined as the reversible color change of some specific classes of chemical compounds, both inorganic and organic, occurring upon their electrochemical reduction and oxidation. This phenomenon was reported primarily in 1815 by the prominent Swedish chemist Jons Jacob Berzelius, who observed a color change in heated WO_3 when exposed to a hydrogen flux. As further outlined by other influential authors, in 1824, the German chemist Friedrich Wohler, famous for being the first to isolate the chemical elements of beryllium and yttrium in their pure metallic forms and for synthesizing the organic compound urea from inorganic reagents, also known as Wohler synthesis, was fascinated by the beauty of WO_3 and its impressive color change upon reaction with sodium which resulted in a gold-like color, likely due to the formation of sodium tungsten bronze [1]. Several other acute observations and notes on the chromism of WO_3 and its electrochemical behavior have been continuously reported over the years. In this context, the term electrochromism was coined in 1961 by J. R. Platt, who observed a color change in some conjugated organic dyes upon application of a strong electric field [2]. However, it was only in 1969, with the seminal paper of Satyen K. Deb on the electrochromic (EC) coloration of WO_3 thin films, that electrochromism began to follow the first steps toward a more systematic investigation taking into account the technological aspects and the applications [3]. Since then, numerous leading scientists have reported significant works on the basic fundaments of electrochromism, contributing to provide a more comprehensive knowledge of the EC phenomena and the electrochemical processes and to the continuous progress of new materials and devices.

With regard to WO_3 and other inorganic EC materials, the renowned book *Handbook of Inorganic Electrochromic Material* of Claes-Göran Granqvist (1st Edition – March 16, 1995, Elsevier) represents a milestone in the literature of inorganic materials covering electrochromism in metal oxides, material preparation, especially via thin film technologies, characterization methods, electro-optical properties, device design, and performance analysis [1]. Although 30 years have passed since the first publication, it still remains a needful and essential book for a

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comprehensive and scrupulous knowledge of the fundaments and basic principles of EC inorganic oxides.

Starting with the electrochromism of metal oxides, especially transition metal oxides, such as tungsten, molybdenum, iridium, titanium, manganese, vanadium, nickel, cobalt, niobium, research efforts have also extended to the exploration of the chromism of organic compounds. These include viologens, phenothiazines, and various dyes and pigments such as orthotolidine, anthraquinone, and Prussian blue (PB). Among these, viologen is one of the dyes that have been more extensively studied for electrochromism, despite becoming more popular as paraquat for its herbicidal properties and high toxicity to mammals, including humans (Figure 1.1). Upon exposure, paraquat causes severe inflammation and can potentially lead to severe lung damage with an irreversible pulmonary fibrosis, also known as paraquat lung, with a high rate of mortality ranging between 60% and 90%. Several murders, and especially numerous suicides, have been indeed committed by using this lethal poison, including the case of Isabella Blow (1958–2007), one of the most influential fashion celebrities of all time. Moreover, the use of paraquat has also been associated with the onset of Parkinson's disease in farm workers. Initially produced and marketed with the trade name of Gramoxone in 1962 by Imperial Chemical Industries (Berkshie, England), it was widely used as a herbicide particularly for weed and glass control. However, due to extreme toxicity, paraquat was withdrawn from the market of the European Union in 2007 and is now only used by licensed applicators in the United States. On the other hand, despite its elevated riskiness, it remains one of the most commonly used herbicides worldwide for its effectiveness and its wide availability at low cost. Viologens have also found applications in the EC technology, resulting in one of the most studied classes of EC organic materials. This is due to their ability to operate at extremely low driving voltages, determining high optical contrast, and fast switching dynamics. The electrochemical behavior of 1,1′-dimethyl-4,4′-bipyridinium, methyl viologen (MV), was first reported by Michaelis and Hill in the early 1930s, who observed the violet color of the reduced state [4]. However, it was in the 1980s that viologens were extensively studied for EC applications, exploiting their ability of giving rise to three differently colored

Figure 1.1 Chemical structure and pictograms of methyl viologen dichloride, more commonly known as the highly toxic and poisonous herbicide paraquat, which is still used in numerous countries for weed and grass control. Source: USFWS Mountain-Prairie/Flickr/CC BY 2.0.

oxidation states: dicationic, monocationic radical (violet), and neutral species (red/orange). The fact that the bipyridinium radical of MV is one of the most stable known organic radicals, it allowed the effective preparation of air-stable solids making it suitable for the fabrication of EC devices. However, the low write-erase efficiency, i.e. the percentage of coloration that can be converted back to its original state, of MV in aqueous-based EC devices, along with the high solubility of the dicationic and radical species leads to the poor device durability and operational failure. To address this issue, various strategies have been employed, such as incorporating long alkyl chains on the nitrogen substituents, in order to obtain solid ECs or favoring the interaction between the viologen and an immobilized polymeric surface or electrode. Interestingly, among the various organic materials, viologen systems are particularly promising for industrial applications and, to date, remain the primary organic EC material used commercially.

Several other organic species with EC properties, including pyrazolines, quinones, carbazoles, and phenylene diamines have been proposed in literature as potentially interesting for practical applications. Recently, new small molecules with interesting redox activity and optical properties have been developed, such as thiophene- and furan-based porphyrinoids, triphenylamine derivatives, and tetrathiafulvenes or dibenzofulvene derivatives. In addition to their high optical contrast in the visible range, dibenzofulvene derivatives also exhibit a near-infrared (NIR) electrochromism across a broad spectrum due to optically induced intervalence charge transfer transitions (IVCTs). This makes them particularly promising for further development of devices and smart window technologies.

About PB, it has been widely used by artists and painters from the early eighteenth century to the end of twentieth century for its impressive deep blue color tone and its incredible magnetic and seductive effect. As seen in Figure 1.2, it is the characteristic

(a) (b)

Figure 1.2 Prussian blue pigment used (a) in Van Gogh's Starry Night on the Rhone (1888, Musée d'Orsay, Parigi) and (b) in The Old Guitarist of Pablo Picasso (1903, Art Institute of Chicago). Source: Musée d'Orsay/Wikimedia Commons/Public Domain, Flickr/Public Domain.

pigment of Picasso's Blue Period, or the color used by Van Gogh to create a moody, dramatic, midnight blue in many famous works, including "Starry Night," "Starry Night on Rhone," and "*Terrace of a Café at Night*," PB was also widely adopted by the painters during Baroque and Rococo periods, and it remains today as an important pigment for paints, lacquers, printing inks, and other color uses. An example is the clock faces of the Elizabeth Tower, more commonly known as Big Ben, sits atop the Palace of Westminster (London, England), which was recently restored to its original 1859 color scheme of PB and gold in order to bring the Tower back to the original design and vision by the architects Charles Barry and Augustus Welby Pugin. The first example of electrochromism for PB thin films was reported in 1978 by Vernon D. Neff from Kent State University (Ohio, United States). He deposited a thin film of PB on platinum electrodes using ferric chloride and potassium ferricyanide, demonstrating the reversibility of coloration [5]. In 1982, Japanese chemists K. Itaya and K. Shibayama developed a more reproducible method for the deposition of PB thin films through the electrochemical reduction of ferric-ferricyanide solution [6].

After these pioneering works, extensive research has been carried out on the structure, chemico-physical and electrochemical properties, and electrochromism of PB and its analogs. Significant results have also been reported on energy-storage properties for applications in batteries and supercapacitors [7–9]. PB undergoes three color changes passing from colorless to blue and then to brown, depending on its redox state. The fully oxidized brown state is unstable, and for practical EC applications, only the reversible switching between colorless and blue can be used, which is associated with the insertion or extraction of balancing cations (preferentially K^+ or NH_4^+). Due to its three-dimensional (3D) zeolite-type structure, PB presents highly reversible intercalation/deintercalation of certain cations, excellent redox activity, and fast charge/discharge processes. This makes PB and its derivatives effective alternatives for the manufacturing of innovative battery cathode/anode materials and supercapacitor electrode materials. Additionally, its ability to capture monovalent metallic cations has been used in the pharmaceutical field for the preparation of drugs that can sequester specific toxic heavy metals, particularly thallium (Tl^+) and radioactive cesium ($^{134}Cs^+$,$^{137}Cs^+$).

In the more recent book *Electrochromic Materials and Devices* edited by Roger J. Mortimer, David R. Rosseinsky, and Paul M. S. Monk (June 2015, Wiley), all materials and devices for electrochromism are discussed in detail, providing a comprehensive bibliography until 2015 with invited contributions from leading experts of the field [10]. This edited book builds upon their earlier monographs on electrochromism, offering the most complete and accurate collection of key issues and basic concepts concerning materials, devices, and applications [11, 12]. Spanning from an in-depth description and discussions of materials, including metal oxides, PB, viologens, conjugated conducting polymers, transition metal coordination complexes and polymers, organic NIR materials, and metal hydrides, to polymer electrolytes, nanostructured EC materials, and associated systems (gyroid-structured electrodes for EC/supercapacitors, plasmonic EC nanocrystals, etc.), it also covers the aspects related to the applications of EC materials, such as smart windows, fabric EC displays, some exemplifying device case studies

(e.g. EC foil, EC glazing in a UK office, and photoelectrochromic devices) alongside environmental impact considerations.

An undoubted and significant contribution to the advancement of the science of organic electronic materials in the EC field was made by John R. Reynolds Research Group at the Georgia Institute of Technology, especially through their focus on electrically conducting and electroactive conjugated polymers. Over the past 40 years, Reynolds and his colleagues have developed new EC polymers by manipulating their optoelectronic and redox features providing deep insights into the charge transport, the electronic structure of conjugated redox-active organic molecules, and the EC mechanism and the electrochemical behavior of organic compounds. A complete treatise on the general concepts and structure–property relationships governing color in conjugated polymers and EC switching control was reported by Anna M. Österholm, D. Eric Shen, and John R. Reynolds in Chapter 6 "Electrochromism in conjugated polymers – strategies for complete and straightforward color control" of the renowned book (last edition) *Handbook of Conducting Polymers* (edited by Reynolds Terje A. Skotheim and Barry C. Thompson) [13]. This chapter provides an in-depth description of soluble, high molecular weight EC polymers focusing on organic systems that switch between colored and clear states. It also addresses experimental parameters (e.g. electrolyte concentration, cell geometry, film thickness, and substrate resistance) that affect device performance, along with a quantitative comparison of material properties. With specific reference to semi-conjugated polymers, also known as conducting plastics, it is worth highlighting that in the last two decades these materials have found relevant industrial exploitation due to the huge advantage of being manufactured as thin solid films through low-cost solution processing techniques, such as inkjet printing. Beginning with the seminal papers (1974–1978) by A. J. Heeger, A. G MacDiarmid, and H. Shirakawa (Nobel Prize in Chemistry, 2000, for the discovery and development of electrically conductive polymers) on the discovery of electrically conducting organic polymers, these revolutionary materials have been applied in different sectors, especially in the electronic field for electronic devices, display technologies (electroluminescent, polymer light-emitting devices), or functional coatings. For example, doped polyaniline (PANI) was used as electromagnetic shielding of electronic circuits or a corrosion inhibitor, while polypyrrole is employed as an active thin layer in various sensing devices. Poly(dialkylfluorene) derivatives are used as emissive layers in full-color displays. Some of these conducting polymers, such as PANIs and poly(ethylenedioxythiophene) (PEDOT), are also suitable for EC and smart windows applications since they possess a whole range of fascinating colors depending on their redox and protonation forms. Additionally, they can be manufactured in large sheets on different substrates (e.g. glass, plastics) and offer unlimited visual angles. Not least important, the concurrent progress in the development of electrolytes and electrodes materials has played a key role in the continuous evolution of EC devices and smart window technologies, passing from those outdated systems using liquid electrolytes to solid-state ones or by employing highly performing, multifunctional, and durable electrodes.

In this book, the key aspects of materials and devices reported in the literature are largely treated, providing a critical discussion on the main challenges affecting materials, device performance, and durability, and how these problems can be overcome in order to fabricate more stable EC smart windows and multifunctional devices. The latter ones are particularly attractive for next-generation EC technologies, responding to the growing market demand of "invisible," portable, and wearable electronic devices. Over the past decade, significant advancements have been made in the development of multifunctional EC devices, such as those realized by combining EC cell with electroluminescent (EL) organic materials for innovative see-through displays that function under various lighting conditions or by the full integration of EC and photovoltaic cells into photoelectrochromic and photovoltachromic devices. Special emphasis is given to systems based on all-solid-state configuration, the rational design of nanostructured materials, and interface engineering, as well as new manufacturing strategies, including those based on simplified single-substrate structures and more "green" manufacturing procedures with low environmental impact and capable of reducing production costs and waste disposal.

In summarizing, along with a wide dissertation on the materials, the analysis of device performance, and discussion on manufacturing procedures, the book explores the energy challenges and environmental impacts. It offers numerous sparks and valuable insights on the emerging and next-generation smart glass technologies having as scenario the new era of Artificial Intelligence (AI) and even more technical society. The book is intended to be a useful source not only for master's and doctoral students but also for researchers in various scientific and technological sectors as well as innovators and designers in the field.