



Perspective of Electrochromic Double Layer Towards Enrichment of Electrochromism: A Review

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Abstract

Electrochromism is the exhibition of reversible optical property changes by certain materials upon administration of voltage across it. Tungsten oxide (WO_3) finds a diverse range of applications because of its exceptional electrochromism. Amidst all applications, an electrochromic device (ECD) can be considered the most prominent application due to energy saving perspective. Although, WO_3 itself has been noticed as an efficient electrochromic layer for EDCs; however, there exists a lot of space and ideas to enhance the electrochromism and hence the efficiency of an ECD. Recently, scientists are paying close attention to hybrid or composite films such as TiO_2/WO_3 and $\text{TiO}_2/\text{V}_2\text{O}_5$. Such hybrid films are known as electrochromic double layer (ECDL). This review article strives to deepen our understanding of ECDL and assess their feasibility in the enrichment of electrochromism in ECDs by replacing a single electrochromic layer with an ECDL toward an energy-saving regime.

Keywords Electrochromism · Transparent conducting oxide (TCO) · Tungsten oxide (WO_3) · Electrochromic double layer (ECDL) · Electrochromic device (ECDs) · Novel electrochromic attribute

1 Introduction

When a mild reversible voltage is put across a material, especially in thin film form, electrochromism occurs, changing the optical glazing from a coloured to a totally bleached condition and vice-versa [1]. Every class of electrochromic (EC) substances has advantages that render it more suited for specific applications. Elevated UV radiation resistance of transition metal oxides (TMOs) is one of them which makes them more suitable for utilised in EC windows created with the goals of saving energy [2]. As remarkable EC materials, TMOs have drawn a lot of attention to study in the last 10 years [3]. TMOs are an intriguing family of solids with a vast range of properties and structures. The properties of metal–oxygen bonds can range from being almost

ionic to being highly covalent or metallic. TMOs in the iron group, involving “nickel oxide, iron oxide, manganese oxide and cobalt oxide” are insulators. “Tungsten oxide (WO_3), niobium oxide, titanium oxide, molybdenum oxide, chromium oxide, vanadium oxide and cerium oxide” on the other hand, have metallic and semiconducting characteristics. The majority of TMOs’ intriguing and unusual features are due to electron–electron interaction in partially filled *d* orbitals. Charge interaction between transition metal atoms which are weakly electronegative and oxygen atoms which are highly electronegative results in the formation of TMOs. There are different oxides formed when transition metals lose various numbers of electrons in the oxygen-atom orbitals. This form of exchange produces a wide diversity of bonds, structures and phases in TMOs. Solid’s outermost or valence electrons are the basis of their electronic properties.

These materials are used in many different areas and have interesting characteristics. One of the remarkable qualities that TMOs display is the semiconductor property. A variety of EC materials, such as tungsten oxide (WO_3) and vanadium pentoxide (V_2O_5), are used in smart windows for their ability to transition between bleached and coloured modes. They are used in sensors, light-emitting diodes (LEDs), and solar cells, among other optoelectronic devices. TMOs have exceptional catalytic capabilities.

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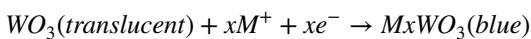
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Without actually being eaten, they may speed up chemical processes. When creating a magnetic storage medium, TMOs play a role.

Magnetic tapes and hard drives make use of iron oxide (Fe_2O_3), more often known as rust. When exposed to light, several TMOs display photochemical activity. In light-induced catalysis, materials such as copper oxide (CuO) and cobalt oxide (Co_3O_4) are used for water splitting and fuel cell applications. Some TMOs are used as colourants in ceramics, paints and plastics. We rely on TMOs for a wide range of applications because of their unique combination of catalytic, semiconducting, magnetic and colour-related characteristics.

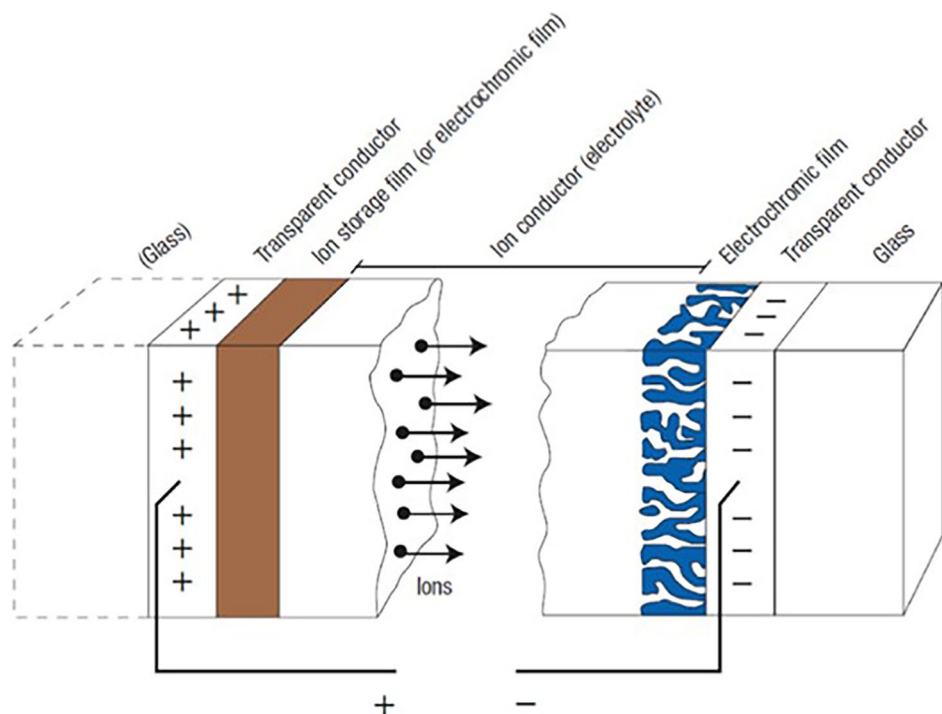
Among all metal oxides, WO_3 has distinguished itself as a special metal oxide due to its extraordinary electrochromic capacity [4]. An electric field that is reversible causes minute ions (H^+ and Li^+) to move into or away from a lattice arrangement of electrochromic oxide (viz. V_2O_5 , WO_3 , TiO_2 and NiO) after implementing extraneous voltage changes. This is reflected as a modulation in optical variables [5–7]. The primary action of electrochromism of WO_3 can be credited to the creation of tungsten bronze (MxWO_3). The equation written below governs this:



where $\text{M} = \text{H}, \text{Li}$ etc.

WO_3 has a wide range of practical uses, including ECDs, automotive anti-glare mirrors, sensors for gases, supercapacitors, solar cells and organic light-emitting diode (OLEDs) [8]. Amidst all applications of WO_3 , ECDs realised as smart window have been finding major focus and commercialization owing to energy-saving capability [9]. Smart windows or electrochromic windows are proving to be efficient towards energy-saving technology as they modulate the transmission of solar heat energy through the building without the need of electronic appliances as per the desirability of the weather conditions [10]. In this concern, it becomes essential to metamorphose the ECD in order to scale it more effectively towards energy-saving regime. ECDs can be generally divided into two groups: (1) configurations of the layered type and (2) configurations of the all-in-one type. A schematic of conventional layered type ECD is shown in Fig. 1. In layered type ECDs, Glass/TCO/EC layer/electrolyte/IS (Ion storage)/TCO/glass is the ECD configuration where the chromophore is placed on or adhered to the working electrode and the electrolyte is integrated as a distinct layer. In most cases, the counter-electrode on the other side of the device has an ion storage layer (Fig. 1), though it can also have EC (i.e., dual-type ECD). As depicted in Fig. 1, when the two electrode substrates are subjected to the proper external voltage, a redox type of reaction takes place, and

Fig. 1 Schematic of ECD depicting the motion of ions and electrons in an outwardly supplied electric field [11]



electrons and/or ions are exchanged amid the EC layer and the ion storage layer via the electrolyte [11]. This type of intercalation and de-intercalation of ions in the EC-layer is responsible for switching of optical glaze of the device between coloration and transparency. This reversible colour change has a direct effect on ECD's capacity to transmit solar radiation. My modulating electric field ECD is capable of regulating the quantity of solar radiation that passes through the building envelope elements (smart window).

In the literature, the term “all-in-one” has been used [12] to explain the symmetric device construction where the EC material and the agent used as redox mediator are diffused in liquid electrolyte [13], solid or semisolid electrolyte [14], and the subsequent EC combination (single layer) is inserted between two electrode substrates in a very straightforward configuration (glass/TCO/EC mixture/TCO/glass). This design is only compatible with EC components that are solvable in electrolytic medium (e.g., viologens). All-in-one ECD architecture has a number of benefits in comparison to alternative EC systems. This architecture facilitates the implementation of streamlining the process of device design. It permits the application of solid, liquid or gel electrolytes. Flexible substrates are compatible with gel electrolytes, enabling the fabrication of a wide range of devices. These devices exhibit potential for forthcoming implementation in smart window, display and other domains.

The EC layer happens to be a prime layer of an ECD. EC layer renders reversible optical property changes from translucent to coloured state in accordance with applied feeble voltage. The demanding energy and environmentally friendly system fulfilment need the advancement of durable and refillable type resources. Consequently, substances that are effectually transforming and preserving energy are immensely needed. In this frame, electrochromic materials get affixed appropriately as it shows reversible optical property changes by application of a feeble electric field across it [15]. Many organic and inorganic materials are utilised as an EC layer, such as TMOs (WO_3 is specifically used), viologens, Prussian blue and conducting polymers. However, the organic electrochromic layer is not feasible for UV-exposure because of its poor durability which restricts its applicability to indoors as smart window, while the inorganic EC materials are cast-off for outdoor smart window [2]. According to the substance utilised, layered-type ECDs can be divided into inorganic metal oxides [16], metal complexes, metal plasmonics-metal/alloy, hybrid materials and organic molecules/conjugated polymers (CPs).

Many metal oxides (such as WO_3 , NiO , MoO_3 and V_2O_5) which have been used as an inorganic EC material [17–19], show colour changes through intercalation/deintercalation of tiny cations (H^+ , Li^+ etc.) into the crystal lattice by inter-valence charge transfer (CT) triggered by a voltage applied.

Although these metal oxide-based ECDs display high optical disparity between the coloured state and bleached state and operate at small voltages with efficient electrical energy consumption, it is still difficult to realise multiple colours of wavelengths that are quite near to one another because of the huge bandgap in metal oxides.

Coordinate bonding occurs in metal complex EC materials between the metal cation and ligands (organic and inorganic species, including polymers, pyridine, porphyrin, CN, halide ions, NH_3 , H_2O and S_2), and reversible CT across the coordinate bond causes colour variations. The realisation of progressive hues is however restricted because the oxidation states of transition metal ions are distinct and only the matching colours may be seen [20]. Organic redox couples can be used to address this issue so that the optical characteristics and accompanying colour rely on the redox states of both the metal ion and the ligand. By electropolymerizing the appropriate monomers in the presence of the metal, the metal–organic polymer complexes are deposited as thin films on the electrode surface; however, this technique is only useful to a smaller surface area of the electrode [21].

The electrodeposition of metals which is reversible including Cu, Ag, Ni, Bi and Mg alloys from their salts in the ECD cell is used in metal plasmonic-based EC materials [22]. Due to the production of diverse size-based optical states and localised surface plasmon resonance (LSPR), metal plasmonic EC materials have been used to produce a variety of hues at low electrical voltage. The optical states of the metal plasmonic materials are momentarily altered. Thus, in ECDs based on metal plasmonic, colour stabilisation depends on precise control and stability of the anticipated shape and size of the nanoparticles, which is accomplished by using constant voltage pulses and an appropriate capping ligand. However, because of their propensity to aggregate, plasmonic nanoparticles' long-term stability in the EC device, in terms of size and form, remains problematic. Following cathodic and anodic polarizations of the EC films, metal alloy-based EC materials change into diverse optical states as a result of redox reaction of the metal alloy. The limitations of this kind of EC materials are the lower optical contrast and thin film stability [23].

Polyaniline (PANI), poly-pyrrole (PPy, conducting polymers), polyaniline derivatives (viologens), and polythiophenes (PThs), among other organic compounds and CPs, have characteristic ultraviolet (UV)-vis absorption spectra that match their redox status [24], making them appropriate for EC uses. More people are interested in using affordable conducting and redox polymers as EC materials because of their quick time of response and elevated contrast ratios. These types of CPs also have a poor UV stability and a varied coloration in their visible spectral range. However, dangerous chemical solvents are used in the multistep procedures needed for the synthesis and purification of organic

EC materials. The unstable and poor conductivity of these EC materials preclude their widespread application [25].

Over the years many scientists have worked on ECDs. David R. Rosseinsky and Roger J. Mortimer published reviews on the chief classes of EC materials used in both prototype and commercial ECDs in 2001. These devices include car mirrors, windows and sunroofs, building windows, displays, printing and frozen-food monitoring. They have tried to scale the applicability of different EC materials, including Viologens, WO_3 , antimony-doped tin oxide (a novel mixed oxide), electroactive polymers, composite systems of electroactive polymers with electro-inert polymers, or with included dyes or dopants and fullerene C_{60} , in the context of an ECD. However, our review article aims to demonstrate the suitability of electrochromic double layer (ECDL) materials, such as TiO_2/WO_3 and $\text{TiO}_2/\text{V}_2\text{O}_5$, for enhancing the electrochromism in ECDs [24]. Poly [3,6-bis (2-ethylenedioxythie nyl)-N-methyl-carbazole] (PBEDOT-NMeCz) and N-propane sulfonated poly(3,4-propylenedioxyppyrrrole) (PProDOP-NPrS) were used as cathodically and anodically coloured layers, respectively, in the construction of ECDs by Irina Schwendeman et al. in 2001. The results demonstrate that employing PProDOP-NPrS as the high-energy band gap polymer has a number of benefits over its carbazole equivalent [26]. Polypyrrrole and polythiophene derivatives were used by De Paoli et al. to develop an ECD. These materials were then coated on flexible, optically transparent plastic electrodes [14]. Stretchable and wearable WO_3 ECDs have been developed by Yan et al. on AgNW elastic conductors [27]. Wang et al. have carried out cutting-edge research in relation to the materials and assembly methods created for polymer-grounded ECDs as an extension to polymer-based ECDs [28]. Eh et al. have also presented their reviews on flexible ECDs [29]. People have also tried to replace TCO (ITO-Indium Tin Oxide)/EC layer by a stacked film of $\text{WO}_3/\text{Ag}/\text{WO}_3$ (WAW) in order to enhance the efficiency and to reduce the cost of an ECD.

We see that over the years majority of the works carried out on ECD are with a single layer of EC. Also, we find that all EC materials are associated with some advantages and disadvantages. None of the EC materials give flawless working in all the conditions. Two electrodes covered with separate electrochromic materials, such as viologen or WO_3 , make up an ECDL. The electrodes change colour in response to redox reactions that occur when a voltage is applied. By outperforming a single electrochromic layer in terms of colour contrast, switching speed and power consumption, the ECDL improves electrochromism. This is due to the fact that the two-layer device can achieve a balance in charge transfer between the electrodes and can exploit both the reflecting and transmissive modes of electrochromism. Smart windows, optical displays and adjustable optical filters are some possible uses for ECDL systems [30].

It has been noticed that judiciously integrating two materials that assist one another can work better towards increasing the efficiency of an ECD as the drawback of one EC material is overcome by the other [31, 32]. Moreover, the suitability of an ECDL for enhancing an ECD's effectiveness, however, has been rarely studied. This article's objective is to assess a variety of studies on ECDLs and determine their suitability towards enhancing the effectiveness of an ECD.

2 Novel Attributes of an EC Material Be Considered Appropriate for ECD

Ideal electrochromic attributes which should be restrained by an EC layer to be feasible in any ECD are as follows:

2.1 Coloration Efficiency

Coloration efficiency (CE) which is nothing but DOD (dynamic optical density change) per unit of induced/retrieved charge density at a certain wavelength can be considered a prime quantity to scale electrochromic behaviour of the thin films developed by different means. Coloration efficiency is defined as the ratio of optical density (ΔOD) at respective injection/ejection charge density (Q_{in}) per unit area (S), which is reflected in Eqs. 1 and 2.

$$\eta = (\Delta\text{OD})_{\lambda}/Q_{in} \quad (1)$$

$$Q_{in} = \int idt/S \quad (2)$$

where $(\Delta\text{OD})_{\lambda} = \log(T_{b\lambda}/T_{c\lambda})$.

$T_{b\lambda}$ and $T_{c\lambda}$ stand for the transmittance of bleached and coloured samples, respectively [33].

An electrochromic thin film with high coloration efficiency is considered a better film over the film which has a lower CE value [34]. Lee et al. have shown that a porous and rough WO_3 film renders better electrochromic properties. Moreover, if it is blended with nanoarchitectures, it can show even better coloration efficiency [35]. Therefore, we need to find such a fabrication technique which readily helps to fabricate nanosculptured porous film.

2.2 Lithium Charge Storage

The intensity of the blue colour acquired by the electrochromic film is directly proportional to the number of Li ions intercalated into the film. Generally, a film having high lithium charge storage tendency is considered a better electrochromic film. It is found that a rough and porous film shows favourability towards high storage capacity of Li ions. Therefore, we need to fabricate a film stack which shows

high lithium charge storage capability and hence could be feasible towards better ECD application [36–38].

2.3 Response Time

The EC response time is another crucial parameter which scale the electrochromic attributes of an EC material and device. A good electrochromic material is expected to have a fast response time. It is broadly understood that electrochromic response time is modulated by two factors: the ion diffusion co-efficient and the length of diffusion path [17]. The earlier one is influenced by chemical structure and the later one depends on the microstructure. Fast response time is advisable for better electrochromic performance. It is been observed that a porous film has a fast response time due to elevated surface area [6, 39–41]. Thus, it is advisable to fabricate porous film for profound ECD application.

2.4 Switching Time

Switching time is another prime factor which decides the electrochromic tendency of an EC material. It is defined as the time that elapses in switching of an electrochromic material from coloured to bleached state and vice versa. It is modulated by ionic diffusion in the electrochromic material. Generally, switching time is given by $\tau \propto L^2 / D$, where L is the film thickness and D is the diffusivity [42]. Higher switching time is advisable for better electrochromic property. It has been observed that a porous film offers higher surface area and channels throughout the film to create shorter distance for charge transportation and to ease the mobility of counterions during its diffusion through the film which enhances the switching time. Thus, we say that porous film could support towards better electrochromic performance [43].

2.5 Optical Contrast Ratio

Optical contrast ratio (ΔT %) is another essential parameter which measures the electrochromic attributes of a material. It is defined as the transmittance difference between the oxidized and reduced states. A material with higher contrast ratio is considered to be a better electrochromic material. A porous film is expected to give a high optical contrast ratio; therefore, a porous film is expected to show a better optical contrast ratio towards better electrochromism [44].

2.6 Cyclic Stability

An ECD is expected to show long-term stability upon switching or cycling for better electrochromic performance. It has been observed that a nanoarchitected porous film shows better cyclic stability and hence it is advisable to opt porous structure for efficient ECDs [44].

2.7 Porosity

A porous film offers large surface-area-to-volume ratio with nanometer magnitude walls for lower diffusion lengths and a higher effectual surface area for large number of intercalation sites [19]. Thus, we can say that a porous structure can better contribute towards electrochromism.

An ECDL which will be scaled in an ECD should have all the novel electrochromic properties such as high coloration efficiency, high contrast ratio, fast response time, fast switching time, high lithium charge storage and optimized thickness.

3 Electrochromic Double Layer (ECDL) Flawlessly Rejuvenating Its Origin Towards Enrichment of Electrochromism

Two crucial factors must be taken into consideration when choosing EC materials [17]: the reaction time, which is constrained by the coefficient of diffusion and the diffusion path length and coloration efficiency (CE), which defines the modulation of optical property with charge insertion or extraction. The EC execution of the WO_3 film is well known to be directly correlated with the degree of crystallisation, as evidenced by the literature [45, 46]. Fully crystalline WO_3 films have a well-ordered, dense structure and a slow rate of electrolyte dissolution. However, they react slowly to applied voltages because there is a larger energy barrier for Li^+ ions to insert, which leads to a slow response time and poor CE. These issues have persisted as the key unresolved issues. WO_3 films which are amorphous have been shown to have the quick response time and maximum CE in the visible wavelength region [47, 48], but their long-term EC stability and repeatability are significantly compromised by structural changes to the flexible amorphous matrix and a high rate of electrolyte dissolution, making them to have reduced commercial worth [45]. However, the majority of the testified WO_3 films have a single crystal structure [49–51]. These films do not meet the requisites of long-term cyclic stability, short response time and high CE. The development of crystalline-amorphous double-layer structured WO_3 -based EC films with short response time and high CE, as well as potential long-term cyclic stability in the electrolytes without any appreciable degradation of performance within given voltages that meet industrial requirements, is an intriguing way to address these deficiencies.

Numerous studies on ECDL using combinations of various electrochromic materials in various morphologies have been conducted over the years. Polypyrrole and polythiophene derivatives were used as the EC materials and were coated over optically transparent plastic electrodes in the construction of an all-polymeric solid-state ECD by De Paoli et al. The electrolyte was a polymer called poly

(epichlorohydrin-co-ethylene oxide) that included LiClO_4 . Results showed that the systems have quick optical response times and strong optical contrast in the visible region [14]. The ability to produce these devices on a wide scale while combining their advantages of electrochromic materials and low-density polymers is what makes them advantageous. It should be highlighted that double-layer polymeric materials used as EC layers are outperforming single layer in terms of performance.

The performance of an amorphous/crystalline double-layered film created by Antonaia et al. was compared to that of single-layered crystalline and amorphous WO_3 . It was observed that the double layer performed better in terms of coloration response and transmittance asymptotic value during the bleaching phase. As a result, their study offered a novel combination of a double layer made of the same material in both amorphous and crystalline phases [52].

A very intriguing study carried out in 2001 by Fanga et al. is thought to be the first effort which acknowledge electrochromic double layer as an effective replacement for single layer in any electrochromic-related applications. In their research, single and double layers of WO_3 and V_2O_5 thin films have been formed on ITO glass utilising the pulsed laser deposition (PLD) method under rich pressure of oxygen and at a substrate heating temperature of 200 °C. The electrochromic performance of $\text{WO}_3(\text{V})/\text{V}_2\text{O}_5(\text{Ti})$ films with two layers was observed to be significantly superior than that of films with only one layer. The durability was tested in the -1.0 to 1.0 V voltage range for 8000 cycles. These double-layer $\text{WO}_3(\text{V})/\text{V}_2\text{O}_5(\text{Ti})$ thin films on ITO have been shown to be excellent cathode thin film candidates for rechargeable batteries and electrochromic devices. The cycle stability and reversibility of $\text{WO}_3(\text{V})$ films have increased because the supplementary top layer of $\text{V}_2\text{O}_5(\text{Ti})$ has a nano-crystalline and c-axis oriented structure, which is appropriate for Li-ions transport. The electrochromic hue of $\text{WO}_3(\text{V})/\text{V}_2\text{O}_5(\text{Ti})$ double-layer thin films is neutral brownish blue. Therefore, the majority of building applications may be appropriate for this double-layer film [53].

In the year 2004, Xu et al. created an EC polymer device that comprises of a laminated two-layer structure sandwiched amid two electrodes. The new design is more modest than the existing ECD, which has an additional component, and comprises of an ITO glass electrode, a cathodic EC polymer film, a solid electrolyte, and an Au-based (or carbon-based) counter electrode (i.e., anodic EC polymer). ProDOT-MePro, a brand-new blue colour-changing EC monomer, and ProDOP-Et₂, a brand-new red colour-changing EC monomer, were both effectively synthesised, and their EC polymer films were created using electro polymerization. For the first time, a fast switchable blue colour device with a high contrast ratio $\% \Delta T$ was created. Compared to an Au-based counter electrode, a carbon-based counter electrode

using ITO can achieve a quicker response time. Additionally, for the first time, the broad temperature ranges are provided under which the switching is stable. This makes the carbon- and Au-based cells suitable for use in extreme environment applications. The EC polymer devices mentioned above offer low switching voltage, an excellent perceived contrast and a memory effect [54].

Thin films were formed on ITO-coated glass and sandwich junctions of transparent solid polymeric electrolyte were used to create small-area ECDs by Pawlicka et al. in the year 2004. $\text{CeO}_2\text{-TiO}_2$ was employed as the counter electrode film, and WO_3 was utilised as the EC film. Starch that had been plasticized with glycerol or ethylene glycol and included LiClO_4 salt was used to create solid polymeric electrolytes. The electrochemical and optical analyses used to analyse the ECD samples, with the latter covering the wavelength range of 200 to 1100 nm, revealed a very positive response. For ECD starch plasticized with glycerol, the alteration in transmittance betwixt coloured and clear states was 30%, and for starch plasticized with ethylene glycol, it was 50%. Additionally, it was noted that applying negative potential caused the ECDs to turn blue after 10 s, and that this procedure was sluggish than that of extraction. The ECDs built with two layers of WO_3 films produced the best performance. These preliminary findings demonstrate the great potential of starch-based electrolytes as materials for electrochromic devices [55].

The opto-electrochemical characteristics of two sol-gel-processed coatings employed in the creation of EC devices and tested in an aqueous KOH electrolyte were the initial focus of the work carried out by Al-Kahlout, Pawlicka and Aegerter. One is an all-transparent NiO-TiO_2 layer with a novel anodic brown coloration, and the other is a $\text{CeO}_2\text{-TiO}_2$ layer that can be utilised as a passive counter electrode. The first layer has much better EC characteristics than pure NiO coatings; however, after around 4000 cycles and after more than 7000 cycles, single layers and double layers both experience corrosion effects. On the other hand, the second layer, $\text{CeO}_2\text{-TiO}_2$, displays extremely reversible behaviour without any corrosion consequences.

With the configuration K-glass/ $\text{NiO}_2\text{-TiO}_2$ /electrolyte/ $\text{CeO}_2\text{-TiO}_2$ /K-glass, these layers were employed to construct $5 \times 10 \text{ cm}^2$ EC windows. The electrolyte used for these windows could either be an aqueous 1 M KOH solution or a newly created gel electrolyte based on starch-impregnated KOH. Additionally, certain advancements have been made employing NiO-TiO_2 EC layers covered by a thin corrosion-resistant layer made of Al_2O_3 , ZrO_2 , TiO_2 and $\text{CeO}_2\text{-TiO}_2$. With the use of opto-electrochemical methods (galvanometry coupled with optical spectroscopy, CV, CA and other techniques), all systems have been investigated and exhibit a brown colour. The starch-KOH gel electrolyte was shown to have superior cycling stability than the aqueous KOH

electrolyte (usually 7000 cycles), although the liquid electrolyte still has a higher overall optical contrast. The cycling stability is increased but the contrast is decreased when a thin layer of corrosion protection is used on top of the NiO-TiO₂ layer. These first findings indicate that a gel electrolyte grounded on a natural substance like starch but infused with KOH is a promising substance to be employed in such ECDs, particularly given its straightforward fabrication process and incredibly low cost [56]. This research solidifies the notion that using an electrochromic double layer rather than a single layer will improve the electrochromic properties of an ECD.

A double EC layer design has been presented by Jang et al. The newly developed structure enables the careful regulation of bistability in EC materials to enable white, green, blue and black states inside a single simple cell. Combining two colour reactions allows for the creation of black colour, which is crucial for high-quality images and addresses a significant current constraint for EC devices [57].

The first electrochromic Bragg mirror (ECBM) using nanoporous multilayers constructed of NiO and WO₃ nanoparticles is described by Redel et al. Tunability can be attained by merging these electrochromic parts in a 1D Bragg mirror tandem configuration since NiO and WO₃ are complimentary in their coloration effects and their subsequent refractive index change. Protons and electrons can move swiftly into and out of the multilayers thanks to the high nano porosity of this ECBM, which changes the balance of Bragg diffraction and intervalence charge transfer optical effects between the layers. A good electrolyte selection ensures that optical characteristics will cycle with little deterioration [58].

The one-pot electrochemical approach used by Qu et al. to create the amorphous- crystalline double-layer structured WO₃ film has the benefit of less cost and straightforward technology. The low barrier of energy for ions to insert in the amorphous layer and superior cycle performance and conductivity in the crystalline layer provide the double-layer structured film with its high CE, robust durability and relatively fast reaction time. Additionally, the growth of nanopores during the electrochemical lithiation/delithiation process results in a film with a greater surface area, which can further speed up response time and boost CE. The films produced during the lithiation/delithiation process under bigger current and with more cycles show a quicker response time and a higher CE [59].

A new electrochromic device (ECD) with better black colour and long-term bistability has been described by Chil Seong Ah et al. By creating a double-layered nanostructure of two unlike EC materials stacked in layers on a single electrode, they were able to achieve these improvements. Even after being turned off for a full hour while in the coloured state, the manufactured ECD retains 90% of the colourful state's light

transmittance. Green, blue and other viologens were gradually immobilised in the lowermost and topmost layers of materials on an electrode to produce a better black. The low voltage causes the green viologens to the first colour, and the high voltage causes the purple viologens to colour. This is due to the fact that green viologens have a lower reduction potential than purple viologens [32].

An "all-inorganic" multicolor electrochromic behaviour is achievable if utilised in a bilayered geometry, according to stepwise spectroscopic and electrochemical experiments on two inorganic films of Co₃O₄ and PB conducted by Chaudhary et al. When implemented, the same exhibits a quick (1.5 s), power-efficient (246 cm²/C), stable (more than 300 switching cycles) and moderate colour contrast (40%) performance, upholding the inorganic electrochromic family's robustness. With a bias of just a few volts, the solid-state gadget that was thusly created can flip between blue, green and brownish colours. The switching mechanism of the device may be the bias-induced redox activity of Co₃O₄ and PB, according to controlled electrochemistry tests carried out on individual electrodes. In situ spectroscopic analyses give researchers more understanding of the device's workings and support the existence of its various colours. Co₃O₄ and PB electrodes can be used to create the unique, quick, stable, "all-inorganic," power-efficient solid-state device that was observed, overcoming the shortcoming of the inorganic materials while keeping their robustness [31].

The hydrothermal method was employed by Reddy et al. to create CeO₂ nanorods with tungsten oxide shells, and the DC magnetron sputtered coating method was successfully used to form CeO₂/WO₃ nanocomposite films on FTO-coated glass substrates. The structural analysis of nanocomposites revealed that the materials had non-stoichiometric amounts of CeO₂ and WO₃. CeO₂/WO₃ nanocomposite films find a suitable place in ECDs for effective performance [60].

Over the time, it has been seen that ECDL has helped to improve electrochromic properties including CE, diffusion co-efficient and optical contrast. Therefore, it becomes crucial to apply double-layered EC material as much as feasible. One application where ECDL can be used effectively is in ECD. Also, it becomes essential to figure out the mechanism behind the improvement of electrochromic behaviour in a double layer.

4 Mechanism That Drives Improvement of Electrochromism in ECDL

The electrochromic materials, namely TiO₂, WO₃, NiO, V₂O₅ and MoO₃, each have advantages and disadvantages of their own. For example, due to qualities including high electrochemical stability, optical modulation, reversibility and scalable low-cost preparation, titanium dioxide (TiO₂)

is regarded as a promising choice for electrochromic smart window applications [61]. However, the poor coloration efficiency, high voltage needs for coloration and delayed switching kinetics of TiO_2 thin films are their inherent limitations in ECDs [62]. The same is true for single-layer fabrications of WO_3 , NiO , V_2O_5 and MoO_3 . Each of these materials has unique benefits and drawbacks [63]. These days, researchers have focused a lot of attention on composites or hybrid films (TiO_2/M , $\text{M} = \text{WO}_3$, NiO , V_2O_5 and MoO_3), which have been effectively created by depositing any of these electrochromic metal oxide layers on the surface of TiO_2 [64, 65]. By overcoming the drawbacks of individual oxide, the different layers in these hybrid films can work together to provide novel capabilities including the memory effect, optical modulation in the near-infrared range and multicolour behaviour [66, 67].

For use in ECDs, WO_3 has been extensively researched. The WO_3 layer on the TiO_2 film has reportedly been shown to improve current density, lower operating potential, increase cycle stability and display long-term memory effects [66, 67]. The presence of additional components significantly affects the electrochromic performance in addition to the structural impact of a single electrochromic layer. The usage of a two-component junction is one practical strategy [68]. In mixed oxide systems, the beneficial qualities of the various elements can complement one another while also minimising their drawbacks [69]. The two-component electrochromic inorganic material composed of TiO_2 and WO_3 , which produces local electronic states 0.7 eV below the conduction band, has received a lot of attention [70].

Using the pulsed laser deposition (PLD) technology, Fang et al. created an electrochromic double layer of $\text{V}_2\text{O}_5/\text{WO}_3$ and $\text{TiO}_2/\text{V}_2\text{O}_5$ at a substrate heating temperature of 200 °C and at a rich oxygen pressure. The structural characterisation reveals that the $\text{V}_2\text{O}_5/\text{WO}_3$ thin films are amorphous in their as-deposited state. At a deposition temperature, as low as 200 °C, highly orientated growth nano-crystalline $\text{TiO}_2/\text{V}_2\text{O}_5$ thin films with polycrystalline orthorhombic structure were effectively created. The cycle stability and reversibility of $\text{V}_2\text{O}_5/\text{WO}_3$ and $\text{TiO}_2/\text{V}_2\text{O}_5$ films have improved because of the additional top layer of film; it showed a nano-crystalline and *c*-axis oriented structure that is ideal for Li-ions transport. These double-layered $\text{V}_2\text{O}_5/\text{WO}_3$ thin films on ITO may make good cathode thin films for rechargeable batteries and ECDs, according to some research. The most effective electrochromic substance, according to studies, is WO_3 [34]. High colouring efficiency, acceptable stability and a reasonably inexpensive price are its benefits. However, neutral grey or bronze is preferable for building window applications than the vivid blue colour of WO_3 thin films in the reduced form. A neutral brownish-blue electrochromic hue

is produced using thin films with double layers of $\text{V}_2\text{O}_5/\text{WO}_3$ and $\text{TiO}_2/\text{V}_2\text{O}_5$. Consequently, this double-layer film may also be appropriate for window applications.

Neto et al. built a prototype ECD with an electrochromic $\text{CeO}_2\text{-TiO}_2$ double layer to investigate the usefulness of ionic liquids at room temperature as electrolytes in electrochemical applications which are illustrated in Fig. 2. Initial research on ECDs with optimised compositions suggests they may serve as effective multifunctional component layers in ECD-based systems [71].

Eren et al. created double-layer flexible ECDs using poly(3,4-ethylenedioxythiophene) PEDOT and WO_3 as electrochromic compounds using situ UV-curing process. Flexible electrochromic performance characteristics including optical contrast and response times were examined using lithium-based salts. Flexible hybrid ECDs with lithium per chlorate (LiClO_4) achieved 38.7% greater optical contrast and 6.44 s quicker colouring time. Increased EC performance is due to increased mobility of the perchlorate anion and improved ionic conductivity of LiClO_4 electrolytes [72].

Lei Zhao and Yuhua Zhang hydrothermally produced WO_3 thin films, then electrodeposited polyaniline (PANI) on them. The WO_3/PANI core-shell structure was ultimately found. Core-shell composite films have much better electrochromic characteristics. Single-material electrochromic films are less cycle stable than core-shell composite films. Additionally, the composite film has a high ion diffusion coefficient and quick electrochromic reaction. In WO_3 film, the Li diffusion coefficient is $4.37 \times 10^{-10} \text{ cm}^2/\text{s}$, whereas in WO_3/PANI film, it is $4.93 \times 10^{-10} \text{ cm}^2/\text{s}$, 13% higher than in the single film. Highly enhanced electrons and ions penetrate the film, optimising its electrochromic characteristics. Results reveal that WO_3/PANI core-shell structure has extensive electrochromic research and usage potential [73].

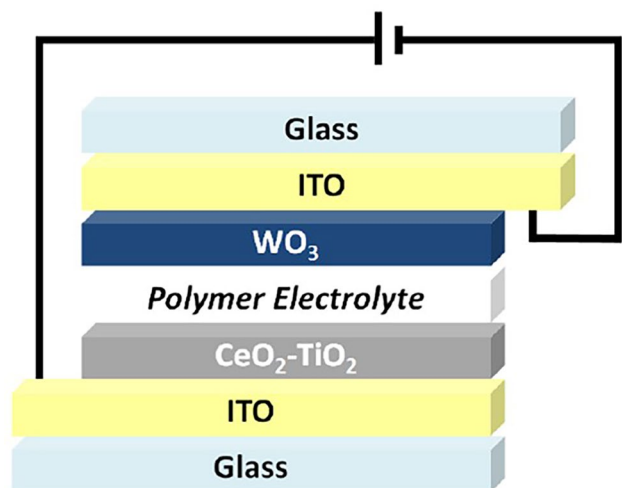


Fig. 2 A schematic of the ECDL structural device [71]

It can be said that the enhanced electrochromism achieved by ECDL is due to the fact that the two layers work together to modify each other's optical characteristics via the exchange of ions and electrons. Ions (e.g., H^+ , Li^+ or Na^+) move from one electrode layer to another in response to an applied voltage, whereas electrons flow in the other way. The electrochromic materials undergo oxidation and reduction as a consequence, which alters their colour and optical band gap. You may also turn the colour change off by switching the voltage's polarity. ECDL outperforms single-layer electrochromic devices in many respects, including contrast, switching speed, power consumption and cycle life. ECDL has a wide range of potential uses, including in sensors, optical filters, smart windows and displays [74].

ECDL is a complicated interfacial area where ions, electrons and molecules interact in the electrode, electrolyte and layer [75]. Electrochromic double layer may be modelled using electric double layer, Butler–Volmer, Nernst–Planck and Poisson–Boltzmann models. Electrochromic process kinetics, thermodynamics and transport may be understood using these models [75].

At the electrode–electrolyte interface, the ECDL model describes charge and potential distribution. The ions are tightly adsorbed or bonded to the electrode surface in a compact layer and loosely scattered in a diffuse layer according to the Poisson–Boltzmann equation [75]. The electric double-layer model may explain ECDL electrochromism by considering: the charge transfer and electric field at the interface modify the electronic states of electrochromic materials, which change the electrode colour [76]. The applied voltage, capacitance, thickness and ion concentration of the electric double layer influence charge transfer and electric field [76]. Dynamic electric double layer reacts to applied potential, electrolyte composition and electrode surface [76]. By influencing ion mass transit and activation energy, the electric double layer may change electrochromic reaction kinetics and efficiency [76]. The electric double-layer model may help us understand the processes and variables that drive ECDL electrochromism and optimise device performance and stability [76].

Butler–Volmer model equations illustrate the link between current density and electrode potential for charge transfer reactions at electrode surfaces. The equation is:

$$j = j_0 [\exp(\alpha_a z F \eta / RT)] - \exp(\alpha_c z F \eta / RT)]$$

Here, j represents current density, j_0 represents exchange current density, α_a and α_c represent anodic and cathodic charge transfer coefficients, z represents electrons in the reaction, F represents Faraday constant, η represents activation overpotential, R characterizes gas constant and T characterizes absolute temperature [77].

By studying the kinetics of redox processes at each electrode, the Butler–Volmer model may explain electrochromism in ECDLs. Electrochromic material colour change is proportional to electrode current density. Device resistance and applied voltage influence electrode potential. The electrode potential minus the redox reaction equilibrium potential is the activation overpotential. Electrochromic material and electrolyte characteristics affect exchange current density and charge transfer coefficients. The ECDL's current–voltage characteristics and colouring efficiency may be calculated by solving the Butler–Volmer equation for each electrode [78].

The mathematical Nernst–Planck model covers charged species transport in a fluid medium under concentration gradients, electric fields and fluid flow. The model uses coupled partial differential equations to connect species fluxes, concentrations and potentials to the applied electric potential or current [79].

The following factors may explain ECDL devices' electrochromic behaviour using the Nernst–Planck model: Electrochromic materials at the electrodes oxidise or reduce according to applied potential or current, changing colour and transferring charge across the interface. Charge transfer produces an electric field in the electrolyte that stimulates ion migration to balance electrode charge. An electrolyte concentration gradient from ion migration drives ion diffusion from high to low concentration locations. Depending on the device's viscosity, pressure and shape, electrolyte fluid flow may alter convection ion transport [78].

The Nernst–Planck model may represent the dynamics of ECDL devices' electrochromic response by solving the equations for species fluxes, concentrations and potentials as functions of time and space under proper boundary and beginning conditions. By considering optical characteristics, power consumption, switching speed and system stability, the model can forecast ECDL device performance and efficiency [78].

Mathematical Poisson–Boltzmann models explain the electric potential and ion concentration in an electrolyte solution near a charged surface. Electrostatic interactions between the ECDL and the electrolyte alter the optical characteristics of the electrochromic material. These theories help explain them [80]. A basic Poisson–Boltzmann model is the Gouy–Chapman model, which assumes that the electrolyte's ions are point charges with the Boltzmann distribution and that the EDL is a flat surface with uniform charge density [81]. To get the electrolyte's electric potential ψ , solve the Poisson–Boltzmann equation:

$$\nabla^2 \Psi = -\rho_e / \epsilon_r \epsilon_o = (F / \epsilon_r \epsilon_o) \sum Z_i C_i \exp(-Z_i F \Psi / RT)$$

Here, ρ_e represents the local electric charge density, ϵ_r represents the solvent's relative permittivity, ϵ_o represents

free space, F is the Faraday constant, z_i represents the valence of the i th ion species, c_i represents its bulk concentration, R is the gas constant and T is the absolute temperature. The Gouy–Chapman model calculates EDL capacitance, which is connected to electrochromic material colour change. This model ignores the ions' limited size, non-Coulombic interactions with the surface and potential adsorption.

The Stern model involves a small layer of specially adsorbed ions at the surface, and the Poisson–Helmholtz–Boltzmann model allows for solvent-mediated, nonelectrostatic ion interactions. These models can better describe ECDL electrostatics and electrochromism [81].

Multiple mechanisms are involved in improving the performance of an ECD comprising of ECDL which are explained below in brief:

a) Capacitive Charging Model

The scientific basis for understanding charge/discharge processes in capacitive materials was provided by the Electric Double Layer (EDL) model, which was introduced by Helmholtz and then revised by Gouy–Chapman–Stern (GCS). There is a surface-controlled mechanism that governs charge storage in ECDs, unlike in batteries where diffusion restrictions in the electrodes play a crucial role. It is because of this quality that ECDs are able to provide rapid charging and discharging. Electric double-layer development at the electrode/electrolyte interface is the basis of the EDL model, which explains the charge storage process. A capacitive effect is produced by the separation of charges (ions) close to the surface of the electrode [82]. The buildup or depletion of charge carriers at the electrode interface causes the electrochromic material's Fermi level to vary in the capacitive charging model. These changes impact the material's optical characteristics by altering its LSPR frequency [83].

b) Faradaic Reactions

The buildup of charges at the electrode–electrolyte interface is the source of the double-layer capacitance. This accumulation of charges prevents ion recombination and enables quick charge and discharge cycles. Ions, the electrode surface and the solvent are the most important participants in this scenario. When compared to the solely capacitive behaviour of the double layer, Faradaic reactions entail the transfer of charge between the electrode and the ions that are present in the electrolyte. Redox processes are responsible for the occurrence of Faradaic reactions. These reactions include ions undergoing reversible oxidation and reduction at the surface of the electrode. The total charge storage capacity is

increased as a result of these processes, which lead to the formation of pseudocapacitance. The Faradaic reaction modifies the absorption spectra of an electrochromic material by oxidising or reducing it, which alters its electronic structure. The introduction of protons and electrons into the lattice of WO_3 causes it to undergo a colour shift from colourless to blue [83].

c) Non-Faradaic Reactions

Charge induction is the process that is involved in non-Faradaic electric double-layer capacitance (EDLC), which does not entail any charge transfer. Occurs at the point where an electrolyte and a polarised metal electrode come into contact with one another. Contributing to the EDLC are ions that have not been particularly adsorbed. To put it simply, it is comparable to the formation of an electric double layer in which charge builds without any chemical processes taking place. It is possible to think of it as the “storage” of charge that is caused by the presence of ions close to the surface of the electrode [84]. In a process known as a non-Faradaic reaction, ions or molecules are adsorbed onto the surface of an electrochromic material, altering its refractive index and dielectric constant. Adsorption of oxygen onto the surface of indium tin oxide (ITO) may cause a colour shift from clear to yellow, for instance [83].

d) Electrochemically Active Functional Molecule-Mediated Mechanism

By using molecules capable of reversible redox reactions, an electrochemically active functional molecule-mediated method may be used to vary the electrochromic material's LSPR frequency. The oxidation of PEDOT's thiophene rings, for instance, may transform the material from blue to transparent [85]. The plasmonic and polaronic processes provide the basis of an additional sort of double-layered electrochromic material. The high light scattering and absorption seen in plasmonic materials are a result of the collective oscillation of free electrons on their surface. These nanoparticles are metals. The creation of polarons—charge carriers paired with lattice distortions—causes organic or inorganic compounds to change colour. These materials are known as polaronic materials. Polaronic and plasmonic materials alter their optical characteristics in distinct ways when a voltage is placed across their electrodes. While polaronic materials may go from a coloured to a bleached state, plasmonic materials can go from a transparent to a scattered state. The end effect is a regulation of light transmission and reflection across two different bands [86].

5 Fabrication Techniques Trending Towards Porous ECDL

Several methods, involving hydrothermal, spin coating, layer-by-layer assembly, electrodeposition and chemical bath deposition (CBD) were employed to add an electrochromic metal oxide layer to the surface of metal oxide films that had already been created [64, 66, 67, 69, 87, 88]. WO₃/TiO₂ nanotube arrays made by combining spray pyrolysis and CBD methods recently demonstrated improved proton storage capacity, a greater contrast ratio, and promising electrochromic performance, according to Song et al. papers [65]. By overlaying a WO₃ layer on the TiO₂ nanotube by electrodeposition, Reyes-Gil et al. created a WO₃/TiO₂ composite film that displayed a high electrochromic contrast of 70%, a significant ion storage capacity of 65 mC/cm² and a quick switching time for coloration and bleaching [66]. According to Yoo et al., WO₃-doped TiO₂ nanotubes showed improved electrochromic characteristics and effective proton intercalation when compared to pure TiO₂ [65]. It is generally agreed that the injection/extraction of electrons and cations is what causes the electrochromic phenomena of various inorganic materials, such as WO₃, Nb₂O₅, MoO₃ and TiO₂ [89].

Significant work has recently been put into enhancing the stability, colour effectiveness, response time and reversibility of inorganic materials' electrochromic characteristics. Since the rate-determining steps of ion intercalation and release are controlled by diffusion and limited to a very thin surface layer of the host materials, the kinetics and magnitude of ion insertion (H⁺, Li⁺, K⁺, etc.) and the electrochromic reaction (colour contrast) are anticipated to be strongly affected by the diffusion length of the ions and the available surface area. As a result, films that are nanoparticulate or nano porous are typically desired [65]. The production of self-organized oxide nanotube (NT) arrays by a straightforward yet optimised electrochemical anodization of a metal substrate offers a utmost sophisticated and practical method among the different techniques for the synthesis

of nanostructures [90]. The many functional features of TiO₂ have drawn a lot of interest to the creation of self-organized TiO₂ nano-tubular formations in particular [91]. Because of the much better-defined geometry of the "one-dimensional" tubular morphology with a much narrower diffusion-length distribution combined with significantly lower losses due to resistivity in the tube walls, the tubes exhibit higher storage capacity, higher cycling stability and also a much more distinct onset potential for switching than TiO₂ nanoparticle layers, where grain and particle boundaries may function as a resistive element [92, 93].

The inclusion of additional components has a considerable impact on the electrochromic performance in addition to the structural effects. The usage of a two-component junction is one practical strategy [94]. In the case of mixed oxide systems, the beneficial properties of the different components can complement one another while simultaneously minimising the drawbacks [92]. The amalgamation of TiO₂ and WO₃, which results in local electronic states 0.7 eV below the conduction band, has received a lot of interest among the countless two-component electrochromic inorganic materials [95].

Over the years, we find that EC double layer has been prepared as a planar film. Although a planar ECDL is showing better EC performance as compared to a single EC layer, there are several thin film properties, modulation of which sharpen the electrochromism in it. One of such thin film property is porosity. The ratio of the volume of voids to the total volume of the film is accounted as porosity. An increase in porosity will lead to an increase in surface area, which will provide more space for ion intercalation and consequently boost electrochromism in the film [96]. In this view, a porous EC double layer will be more scopious. Here we will discuss the scope of different thin film fabrication techniques to produce a porous film which can elevate its usability for double-layer formation. Thin film deposition techniques can be broadly classified into two categories namely physical deposition and chemical deposition. A

Table 1 Thin film deposition methods

Physical deposition	Chemical deposition
1. Evaporation techniques	1. Chemical bath deposition
a. Vacuum thermal evaporation	2. Spray pyrolysis technique
b. Electron beam evaporation	3. Sol-gel Technique
c. Laser beam evaporation	4. Plating
d. Arc evaporation	a. Electroplating
e. Molecular beam epitaxy	b. Electroless plating
f. Ion plating evaporation	5. Chemical vapor deposition (CVD)
2. Sputtering technique	a. Low pressure (LPCVD)
b. Direct current sputtering (DC sputtering)	c. Plasma enhanced (PECVD)
d. Radio frequency sputtering (RF sputtering)	c. Atomic layer deposition (ALD)

broad prospect of thin film deposition technique is summarised in Table 1.

5.1 Physical Deposition Technique

5.1.1 Evaporation Technique

This is one of the most common techniques for material deposition in thin film form. It entails converting a substance from a solid to a gas and back again by coming into contact with a vapour phase in a comparatively cooler environment on a substrate [97].

5.1.2 Vacuum Thermal Evaporation Technique

Two essential components of the thermal evaporation process are the application of a potential difference to the substrate at medium- or higher-vacuum levels ranging from 10^{-5} to 10^{-9} mbar and the use of thermally evaporated material. Figure 3 is a schematic diagram for thermal evaporation.

The vacuum thermal evaporation method offers a vast prospect in making the film porous. The process parameters that may be regulated to help create a porous layer in the vacuum thermal evaporation method include the substrate's nature and temperature, the distance between the source and the substrate, the rate of deposition and the ventilation of an inert gas into the chamber.

A fast nucleation site arises when an atom collides with a low substrate temperature, cools down, loses kinetic energy and has limited mobility. As a result, a thick film develops. However, when the substrate temperature is high, the hitting

particles' increased mobility prevents them from settling down quickly, delaying the formation of the nucleation site, and the resulting films' graininess and porosity will be moderately high. It has been discovered that lower deposition rates result in less dense and porous film whereas greater deposition rates produce more dense films. This could be explained by the fact that increased deposition rates give nucleation sites less time to form, leading to dense film formation with continuous inflow of incoming flux of vaporised target atoms. On the other hand, slower settlement of the incoming flow of vaporised source atoms leads to a more porous film because it gives the nucleation site more time to develop [99]. We can infer from the study of Devika M. et al. that a poly-crystalline ITO-coated CORNING 7059 glass substrate may be a more advantageous substrate for the production of porous WO_3 film [100]. Increased source-to-substrate distance will support delayed nucleation at substrate and consequently leads to porous film. In addition to substrate temperature and deposition rate, ventilating an inert gas (argon) at a high pressure inside the chamber is an exciting approach to add granularity and porosity to thin films. Via the ventilation of inert gas inside the chamber, the thermodynamics of the particles striking the substrate are altered. When the mean free route of the argon gas falls below the chamber dimensions, sublimated particles begin to collide with the gas' atoms. As a result, they are diverted from the gas' rectilinear path and skip the substrate. As a result of the likelihood that a sublimated particle will collide with both argon particles and itself in this situation, source atoms will first nucleate before reaching the substrate. The formation of granular and porous films is the outcome of advanced nucleation [101].

As stated above, we see that the vacuum thermal evaporation technique has a lot of avenues in making the film porous. Although no work has been reported on EC double layer using vacuum thermal evaporation technique, we can make use of the legacy of this technique for making porous EC double layer which finds vast applications.

5.1.3 Electron-Beam Evaporation Technique

A further kind of physical deposition is this kind of evaporation, which is seen in Fig. 4 and involves producing an intense electron beam from a filament, guiding it via electric and magnetic fields, and then impacting the target and vaporising it in a vacuum environment [102].

The electron beam evaporation technique also offers a lot of scope for porous film fabrication. The process conditions such as substrate temperature and deposition rate are the key factors in modulating the film towards more porous texture. A work carried out by Bujji Babu and Madhuri has shown that increased substrate temperature will help towards getting more rougher and porous film

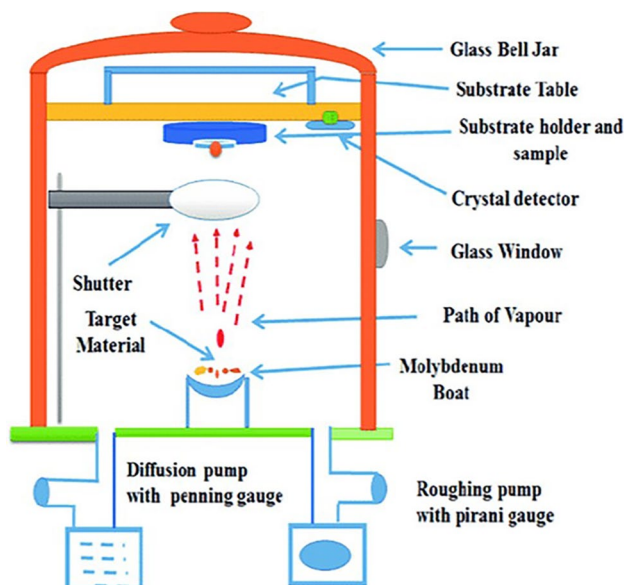


Fig. 3 Schematic of Vacuum thermal evaporation technique [98]

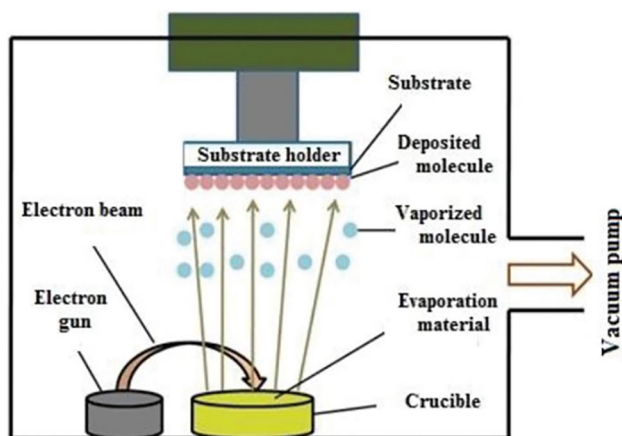


Fig. 4 Schematic of Electron beam evaporation technique [103]

due to increased mobility of the evaporated species [104]. Deposition rate also plays a major role in film texture. A modest deposition rate will offer an ideal film towards better electrochromism. This is because modest deposition rate will offer suitable environment for the film to grow modestly porous due to delayed nucleation [105].

Above-stated benefits of the electron beam evaporation technique can be utilised in the fabrication of porous EC double layer which may find abundant usefulness in many applications.

5.1.4 Laser Beam Evaporation (Pulsed-Laser Deposition)

PLD is another kind of physical deposition for the thin-film coating system. As illustrated in Fig. 5, a beam of laser is cast-off to ablate the material in a vacuum chamber before it is utilised to deposit thin layers on the substrate [106].

To ablate the target, various types of sources producing laser are being utilised. The utmost popular sources are the XeCl (308 nm), KrF (248 nm) and Nd-YAG lasers. Various

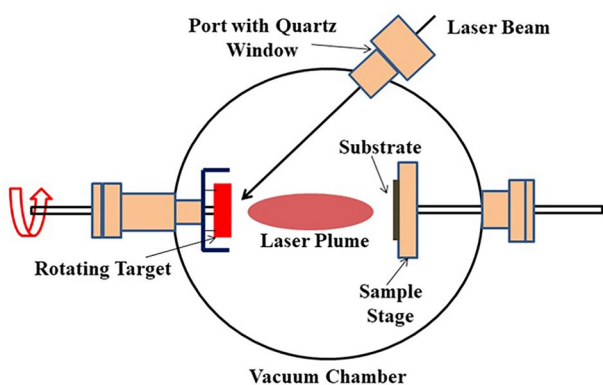


Fig. 5 Schematic of PLD [107]

substrates may get various deposits from the plume formed when the laser beam strikes the target material. Ionised species as well as neutral- and ground-state atoms could be present in the generated plume. Metal oxides are deposited using oxygen in the case of metal oxide thin films. The PLD's thin-film quality is influenced by a number of factors, including the laser's intensity, pulse duration, ambient gas pressure and target-to-substrate distance [108]. The quality of the thin film is controlled by a number of variables, including target-to-substrate distance, laser energy, ambient gas pressure and pulse duration. Laser evaporation has an advantage over other physical deposition technologies due to its quick time of deposition and synchronisation with oxygen and other inert gases [109].

When it comes to completely transferring the stoichiometry from the target to the substrate, PLD can be useful. The incompatibility of partial vapour pressures and sputtering yield prevents a full transfer of stoichiometry from target to substrate, in contrast to other fabrication methods like evaporation and sputtering. Full transference of stoichiometry occurs as a result of the laser's extreme heating of the target material at a temperature rate of around 1012 K/s [110]. Based on the findings of complete stoichiometry transfer, it can be inferred that materials possessing the perovskite structure, characterised by the formation of tunnels within discrete octahedrons and a three-dimensional nanoporous configuration, are amenable to deposition using complete stoichiometry transfer. This process preserves the nanoporous structure of the deposited film, enabling its utilisation in diverse applications. In contrast to conventional thin film production methods, where we must adjust the substrate's temperature to modify the film's properties, the PLD method additionally offers the potential to modify the energy of the ablated particles, which can affect the texture of the resulting film [111].

The electrochromic attributes of Ni^{3+} containing improved NiO thin films were examined with the aim of enhancing the performances of neutral colour devices rooted on the combination of WO_3 and NiO thin films. Films with greater porosity displayed improved EC performance [112]. Liu et al. have demonstrated the consequence of laser power density on the morphology of the WO_3 film. Their idea can be utilised in creating porous EC double layer for extending its usefulness in different applications [113]. Lethy et al. have created porous WO_3 films using PLD technique with increased substrate temperature [114]. WO_3 has been developed by Elisabeth M. Preiß et al. utilising the picosecond pulsed laser deposition process. They created different WO_3 films at rising pressures of oxygen while the film was being deposited. It has been discovered that porosity rises as oxygen pressure rises. Consequently, WO_3 films with extremely porous texture suited for gas sensing applications for CO and NO_2 can be developed by adjusting the oxygen pressure

during PLD process [115]. Thus, we find that the PLD technique is an appropriate technique for fabricating porous EC double layer.

5.1.5 Molecular Beam Epitaxy

The method of producing thin, epitaxial films of a wide range of materials, including oxides, semiconductors and metals, is known as molecular beam epitaxy (MBE). To the development of compound semiconductors, it was initially utilised. Due in significant part to the tremendous technological value of such materials to the electronics sector, it is still the most typical application. In this procedure, heated crystals that have already undergone processing to generate a virtually atomically pristine surface are incident with beams of atoms or molecules in an ultra-high vacuum environment. The arriving component atoms create an epitaxial film, or crystalline layer, in registry with the substrate. The composition of these films can be quickly altered, resulting in crystalline surfaces that are practically atomically abrupt. As a result, it has become feasible to create a wide variety of distinctive structures, such as superlattices, lasers, and quantum well devices, all of which profit from the careful control of composition during growth. MBE structures closely resemble the idealised models utilised in solid state theory due to the purity of the growing environment and the exact control over composition [116]. Figure 6 shows a schematic of the molecular beam epitaxy technique.

Although this technique has not been used extensively in the fabrication of porous EC material, it can be utilised

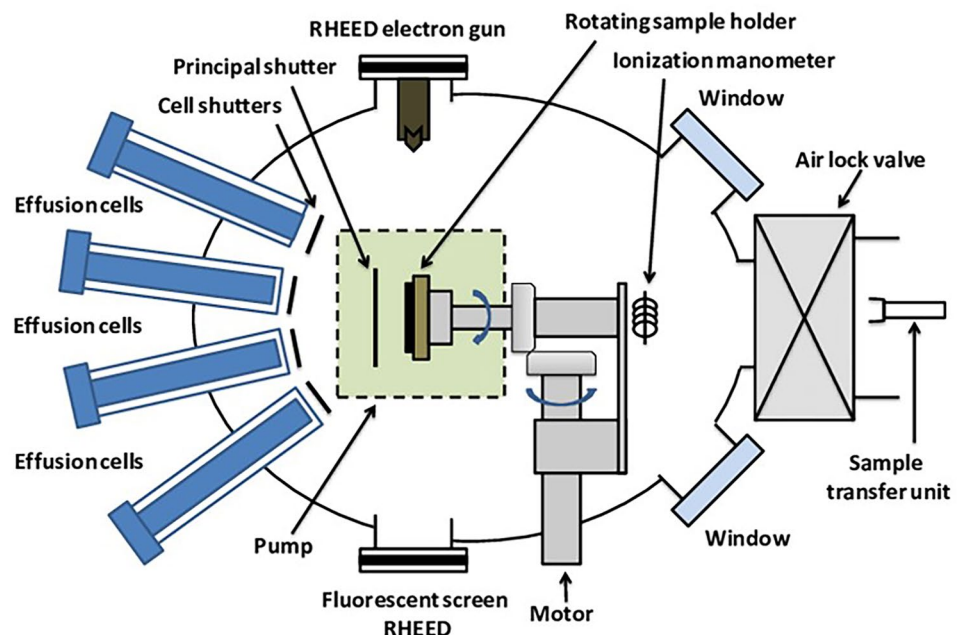
potentially due to the purity of the growing environment and the exact control over composition.

5.1.6 Ion Plating Evaporation

Ion plating refers to atomistic film deposition procedures in which a flow of high-energy ions is supplied to the substrate in order to significantly sputter the surface both before and after the film is formed. The primary benefits of ion plating in terms of adhesion are as follows: (1) the capability to effectively remove impurities from the surface and maintain its cleanliness until the film begins to form, (2) delivering a substantial amount of energy to the substrate surface, resulting in a high surface temperature without requiring the entire substrate to be heated. This, in turn, enhances diffusion, chemical reactions, and other related processes, and (3) modifying the surface and interfacial structure by introducing high concentrations of defects, physically blending the film, and so forth. Where traditional deposition procedures produce poor results in some systems, ion plating is particularly effective at achieving good adherence. The extremely strong “throwing strength” of the depositing substance is another feature of the ion plating process [118].

There are many reports of fabricating porous EC films using ion plating technique [119–121]. Apart from these, in view of above-stated benefits, we can say that ion plating can be an ideal technique to fabricate clean and porous film with better adhesion. This is because substrate is sputter cleaned before film deposition, and high energy flux preheat the substrate which delays the nucleation and makes the film porous.

Fig. 6 Schematic of molecular beam epitaxy [117]



5.2 Sputtering

One of the most cutting-edge techniques for producing thin films is sputtering. An extremely vacuumized chamber with a pressure value of 3×10^{-6} mbar makes up the sputtering system. The target and substrate holders are both stored inside the chamber, with the target being located at the bottom and top, respectively. To create gaseous plasma, an elevated potential difference across the target and substrate is supplied in the chamber at a certain pressure. Once the plasma is created, the target atoms are dislodged by bombarding them with Ar^+ ions via the transfer of momentum from powerfully moving Ar^+ ions. The displaced atoms travel in the direction of the substrate and deposit as a thin coating. A schematic of the sputtering process is illustrated in Fig. 7.

Furthermore, apart from the explicitly mentioned process variables that were identified to enhance the porosity of EC film in the aforementioned technique, such as post-annealing, elevated substrate temperature, increase in source-to-substrate distance and nature of the substance, another process variable that is expected to augment the porosity of EC films is the oxygen partial pressure and selection of the appropriate gas for plasma generation. The concept of oxygen partial pressure in enhancing the porosity of an EC film was well supported by a work carried out by Karup-samy. He created WO_3 films and post-annealed them at 450°C using varied oxygen partial pressures. He noticed that grain size and crystallinity decreased as partial pressure increased. Particularly, a higher colouring efficiency of $58 \text{ cm}^2/\text{C}$ is noted at a partial pressure of oxygen around 2×10^{-3} mbar. You can consider this partial pressure to be the optimal partial pressure for increasing electrochromism in WO_3 films. Reduced bulk density and porosity of the film will be supported by lower crystallinity and grain size, which

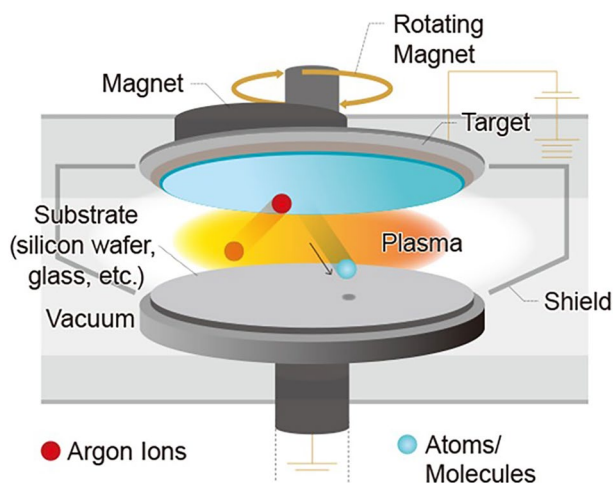


Fig. 7 Schematic of sputtering

increase pore density [122]. Choosing the right sputtering gas is another technique to alter the porosity of EC thin films during the sputtering process. The interplay between the physical properties of the gas atoms used for sputtering and the ability of the target atoms to move influences both the shadowing effect and the porosity of the film. According to a study done by Godinho et al., helium has a considerably larger pore size than Ar when used as a sputtering gas [123]. Thus, we can say that He will be a better sputtering gas for producing porous EC film.

Thus, sputtering can be considered a potential technique to fabricate porous double-layered EC film in view of the added advantage of modulating film porosity by adjusting oxygen partial pressure and selecting suitable sputtering gas.

5.3 GLAD Recourse for Porous ECDL

In many different applications, thin films serve as simple, homogeneous coatings, while lithographically treated thin films serve as patterned layers in micro and optoelectronic circuits. A developing technique for creating thin films involves changing the film microstructure during the deposition or fabrication process, rather than relying only on uniformity or patterning after deposition, to achieve desired functionality has been emerging. Glancing angle deposition (GLAD) is one of such approach. The GLAD physical vapour deposition process rotates the substrate about two axes rather than holding it fixed in place parallel to the incoming flux's direction [124]. A diagram of GLAD technique is illustrated in Fig. 8.

As shown in Fig. 7, α is the incident flux angle w.r.t normal to the substrate. Shadowing effect is the key factor in

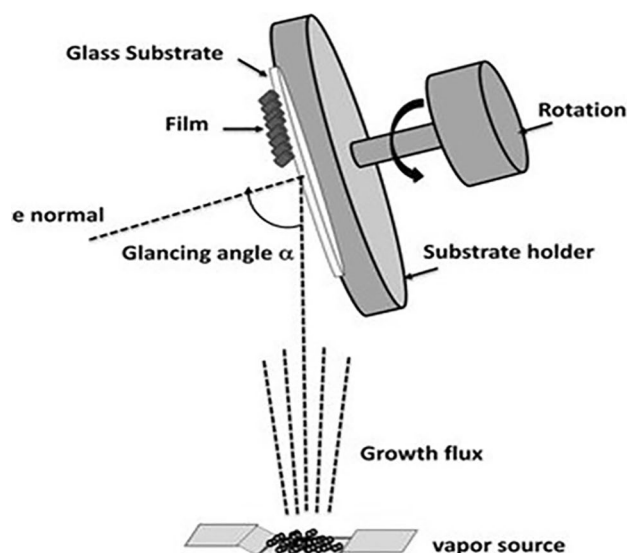


Fig. 8 Schematic of GLAD [125]

GALD technique which supports in enhancing the porosity of the film with increasing incident flux angle. Apart from the incident flux angle, if the substrate is rotated with a fine sweep about its axis, it gives an additional advantage of engineering the columnar structure into spirals, polygonal helices, chevrons, etc. [126].

As stated above, GLAD has a supreme potential of making the film porous by virtue of shadowing effect. It is so flexible that it gets integrated with all PVD techniques and opens a pathway to create a porous film. Therefore, it can be visualised that the GLAD technique can be incorporated with any of the PVD technique to produce porous EC double layer for ECD applications. GLAD has proved its legacy in creating porous EC film which is evidential from the works of Sakkas et al., Beydaghyan et al., Horprathum et al. etc. [102, 127, 128]. Thus, we can predict that GLAD incorporated with any of the PVD technique can be really a helpful way to create porous ECDL which can be more suitable in ECD application.

5.4 Chemical Deposition

Although the previously stated physical methods for producing thin films have good quality and functionalizing capabilities, they are also quite expensive and may need a lot of material. Chemical deposition techniques are utilised frequently over the world because it is important to manufacture good thin films at a reasonable cost. These approaches are cost-effective and provide movies of superior quality. The majority of them do not need expensive equipment. The chemical composition of the solution, pH level, viscosity, and other parameters together have a substantial influence on the process of chemical deposition. The most common ways to make chemical deposition are the sol-gel method, electrodeposition, chemical bath deposition, spray pyrolysis and chemical vapour deposition (CVD) method.

5.4.1 Chemical Bath Deposition (CBD)

The term “chemical bath deposition method” can also refer to controlled precipitations or the solution growth technique. This technique for depositing films on a substrate is the oldest. Chalcogenide and metal oxide films are often prepared using the solution growth process. Moreover, lower temperatures can be used to carry out the deposition. In the solution growth technique, ligands must complex the metal ion precursor solution. Ammonia solution, triethanolamine, ethylene-diamine-tetraacetic acid (EDTA), citric acid and other ingredients are almost all necessary to create the complex solution. The addition of the anions ought to occur after the complexation is finished. To deposit the chalcogenides,

these anions come from solutions of thiourea, thioacetamide, thiosulfate and sodium sulphide as sources of sulphur anions or selenourea and sodium selenosulfate as sources of selenium anions. Substrates are positioned into the solution in a vertical, horizontal, or particular position and held there until the desired film thickness is achieved. In comparison to chalcogenides, oxide coatings are deposited in a very different way typically, the metal hydroxide films are formed as a consequence of the substrate being submerged in the solution at the necessary temperature, which may vary from 60 to 100 °C. This occurs after the complexation process has been finished by altering the pH value. The annealing procedure might then convert the hydroxide coating to oxide [129]. A schematic of chemical bath deposition is shown in Fig. 9.

The CBD method is a useful method since it is affordable, low-temperature and suitable for large-area deposition. On the other hand, the films that were created by this chemical process had distinct differences in terms of their stoichiometry, structure, crystallinity and crystallite numbers. Films that have been chemically deposited must additionally be subjected to a heat treatment in order to achieve the desired results of increasing their adhesion to the substrate and ensuring their structural stability. Inamdar et al. have fabricated amorphous porous nickel hydroxide thin films using the CBD technique [130]. As a counter electrode for a NiO/WO₃ complementary electrochromic window, Huang et al. have prepared a porous NiO thin film [131].

Thus, we see that the CBD technique can be useful for producing porous EC films which can be useful for many EC applications.

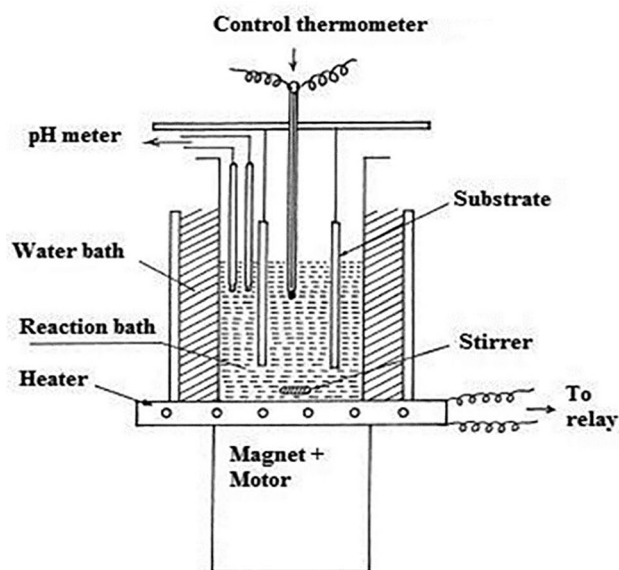


Fig. 9 Schematic of Chemical bath deposition [129]

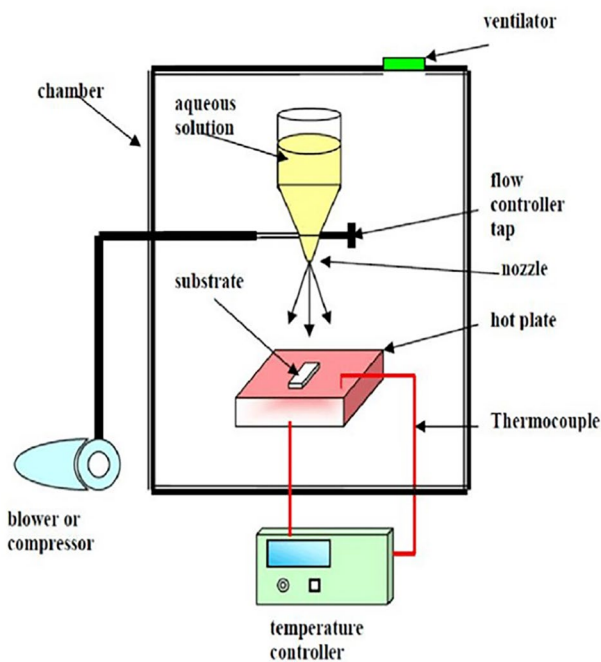


Fig. 10 Schematic of spray pyrolysis [133]

5.4.2 Spray Pyrolysis

Deposition parameters are controlled in spray pyrolysis to create thick or porous films and powders. The precursor solution is atomized and poured directly over the heated substrate to produce the film. The method may produce thin films and ternary chalcogenides from groups I-III-VI, II-III-VI, II-VI-VI and V-II-VI. Spray pyrolysis, a bottom-up aerosol processing technique, atomizes chemical precursors into aerosol droplets in a gas medium. Aerosols in a heated reactor evaporate and create ultrafine particles or thin films. This technique has synthesised particles and multi-component compounds. It is cheaper and simpler than gas-to-particle conversion. Spray pyrolysis may produce nanoscale metal

oxides such as Al_2O_3 , ZnO and ZrO_2 , for example. Flammable spray pyrolysis involves dissolving or combining nanoparticle precursors with flammable liquids or solvents like toluene and ethanol and spraying the mixture onto the combustion flame. The spray burns to generate metal oxide or nanosized metal under experimental circumstances. Flame pyrolysis may produce spinels, metal oxide nano powder like TiO_2 and Al_2O_3 and metal alloys. This technique has cheap cost and high output rates [132]. A schematic of spray pyrolysis is given in Fig. 10.

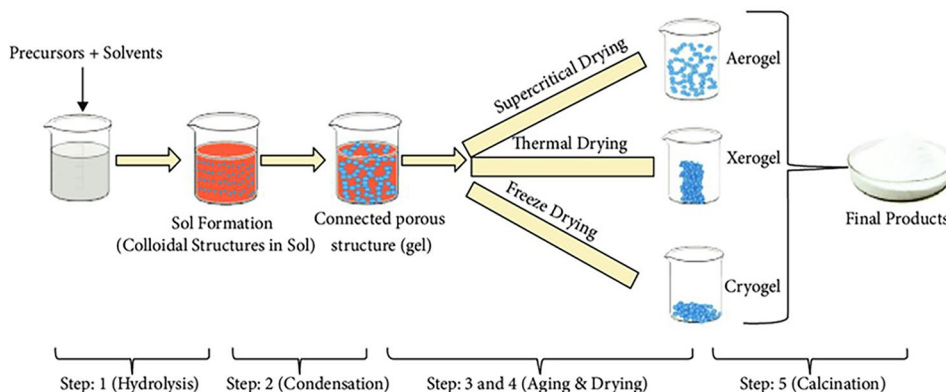
Although it efficiently synthesises metal oxide film forms for supercapacitors, gas sensors, optoelectronic devices and solar cells [132], not much information is available on “porous electrochromic double layer”.

5.4.3 Sol-Gel Technique

A solid substance which can be either glassy or ceramic may be created from a tiny molecule, using the sol-gel technique, a wet chemical process. The first step is to create a colloidal solution (sol), which is the building block for a polymer or particle network with a gel-like structure. After the gel has been dried or calcined, it may be moulded into films, fibres, powders or even monoliths [134]. One low-cost and low-temperature approach of controlling the microstructure and chemical content of a product is the sol-gel process. Optical, electrical, biosensor, medicinal and separation technology are just a few of the many fields that benefit from sol-gel materials [135]. A schematic of the sol-gel method is given in Fig. 11.

The sol-gel technology may be classified into two distinct streams: the conventional sol-gel technique and the non-classical sol-gel approach. The sol-gel technique, also known as “soft chemistry”, is a traditional method. It differs from traditional industrial techniques used in glass and ceramic production, which usually include very high temperatures. This methodology involves the synthesis of solid materials, namely metal oxides, by the utilisation of solution-state precursors. The essential procedures include

Fig. 11 Schematic of sol-gel method [134]



the following stages: sol creation, gel formation, drying and shrinking and heat treatment. The mechanical characteristics, structural stability and densification of the material are improved by a further fire process, which involves polycondensation, sintering and grain development. The process has several benefits, including the ability to achieve densification at reduced temperatures, precise manipulation of chemical composition and suitability for various materials such as thin films and ceramics. The use of non-classical sol–gel techniques involves a wider array of synthesis methods that extend beyond the conventional approach. These methods include the process of breaking down metal alkoxides by hydrolysis and condensation, resulting in the creation of solid substances (such as metal oxides) from precursors in a solution state. Advanced catalytic formulations with structural homogeneity are designed using non-classical sol–gel techniques. These materials are used in several fields such as optics, electronics, energy, space exploration, sensors, medicine (specifically controlled medication release) and separation technologies (such as chromatography). The use of sol–gel technology is also seen in the production of coatings, whereby a stationary sol undergoes a transformation into a cohesive gel network.

In conclusion, both classical and non-classical sol–gel processes possess distinct benefits and have significant importance in the field of material science and engineering.

Though it is a very proficient technique for thin film fabrication, no literature is available for making porous electrochromic double layer.

5.4.4 Chemical Vapour Deposition (CVD)

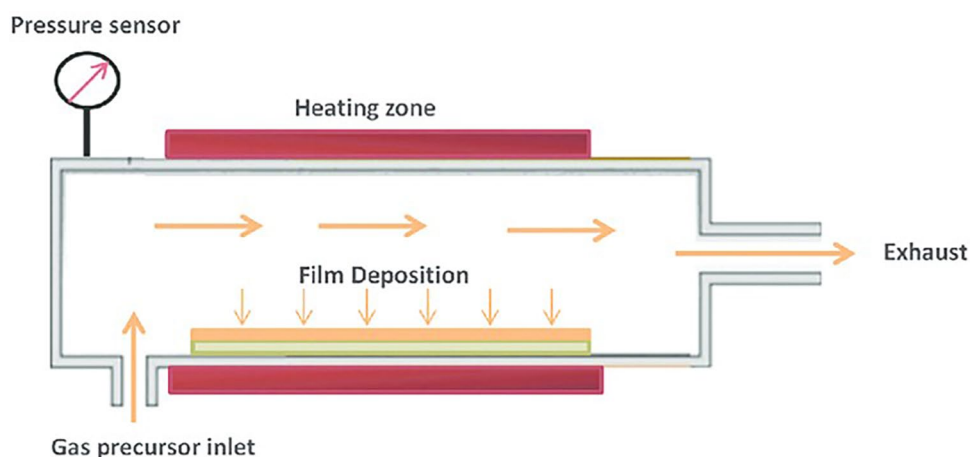
CVD is a method for depositing thin layers of different materials onto a base. The semiconductor industry often employs this method for the production of thin films¹. Conventional CVD involves exposing the substrate (wafer) to volatile precursors, which then react and/or breakdown on the surface

of the substrate to create the desired deposit. Gas movement through the reaction chamber¹ also removes volatile by-products, which are created often. Microfabrication processes often include the use of CVD for the purpose of depositing materials in a variety of morphologies, including monocrystalline, polycrystalline, amorphous and epitaxial. A wide range of materials, including silicon (in various forms such as oxide, carbide, nitride and oxynitride), carbon (in various forms such as fibre, nanofibers, nanotubes, diamond and graphene), fluorocarbons, filaments, tungsten, titanium nitride and a variety of high- κ dielectrics, are included in this category of materials. Various film qualities may be achieved by varying the pressure, temperature and precursor types used in CVD. The semiconductor industry heavily relies on CVD to manufacture thin films for many devices, including sensors, solar cells, LEDs and transistors. Nanomaterials like graphene and carbon nanotubes are also made via CVD. CVD is an effective and flexible method for fabricating thin films [136]. There are two main ways to classify this procedure: thermally triggered CVD and plasma-enhanced CVD. A scheme of CVD is illustrated in Fig. 12

CVD is a viable option for fabricating electrochromic double layers with pores. Reversible colour shifts from translucent to dark blue may be seen in a porous electrochromic double layer composed of a composite film of nickel oxide (NiO) and vanadium pentoxide (V_2O_5). The electrochromic cathode is the NiO layer, while the ion storage anode is the V_2O_5 layer. A higher surface area for dye adsorption and light scattering may be achieved by increasing the porosity of the V_2O_5 layer, while the porosity of the NiO layer can boost the transport of ions and electrons [138, 139].

The usage of a double-layer porous ZnO film as a photoanode in dye-sensitized solar cells (DSSCs)⁴ is another example. Thicker ZnO layers with larger particles enhance electron transport and light scattering, whereas thinner ZnO layers with smaller particles enhance dye loading. By balancing these elements, the double-layer structure outperforms the single-layer structure in terms of power conversion efficiency [140].

Fig. 12 Schematic of CVD technique [137]



CVD offers a flexible and scalable way to deposit different materials with adjustable characteristics, making it a potentially useful tool for fabricating porous ECDLs. Composite structures that improve electrochromic performance may be created by combining CVD with additional processes like electrodeposition or polymerization.

6 Future Scope for ECDL

A double-layer ECD has two layers of electrochromic materials with distinct colours and opposing redox reactions. A tiny voltage across an ECDL changes its colour and optical characteristics. ECDL may be used in smart windows, displays, electronic skins, energy storage and wearables. Future difficulties and potential for the electrochromic double layer are:

Hydrogen fuel cells instead of liquid crystals may improve electrochromic materials and electrolytes. Create flexible, stretchy electrochromic devices for fabric, plastic and metal applications. Integrating electrochromic devices with smart technologies like sensors, actuators and communication systems enables multipurpose and interactive gadgets. Developing electrochromic effects and methods, including thermochromism, photochromism and magnetochromism, to enhance device colour range and usefulness [128].

Porous ECDL might be used in smart windows, displays and adaptive camouflage. Polystyrene as an intermediate layer improves nano porosity WO_3 films' electrochromic properties. The polystyrene layer creates a porous network that increases WO_3 film surface area and ion transport, improving colouring efficiency, durability and reaction speed [141].

SnO_2 nanosheet scaffold improves cycle stability and optical modification of electrochromic materials including PANI, V_2O_5 and WO_3 . The SnO_2 scaffold improves electrochromic material-substrate adhesion, electrochemical active area and ion transport [142].

The creation of eco-friendly, low-cost and scalable porous ECDL devices. Current technologies including spin coating, sputtering and sol-gel have cost, energy and consistency issues. Electrospinning, printing and self-assembly may enable high-performance, large-area devices [141]. Thus, it is seen that ECDL technology promises smart and adaptable solutions for diverse applications. It needs further study and development to overcome its limits and obstacles.

7 Conclusion

ECDL is a complex interfacial region that involves the interaction of ions, electrons and molecules in the electrode, electrolyte and electrochromic layer. ECDL can be modelled by different approaches, such as the electric double layer model, the Butler–Volmer model, the Nernst–Planck model and the

Poisson–Boltzmann model. These models can help to understand the kinetics, thermodynamics and transport phenomena of electrochromic processes. ECDL can be influenced by many factors, such as the electrode material, the electrolyte composition, the electrochromic layer thickness, the applied potential, the temperature and the humidity. These factors can affect the performance, stability and durability of ECDs. When voltage is applied, ions travel across layers, changing colour concurrently. The contrast and optical density of the gadget increase electrochromism. Different fabrication techniques can be utilised positively to prepare ECDL which can be deployed in an ECD. Moreover, if we try our hand on utilising the different fabrication techniques towards porous ECDL, then it will be more scipious as it increases the surface area for more charge intercalation/deintercalation process. Thus, we see that porous ECDL is a promising research field that can lead to the development of novel materials, devices and applications for energy efficiency, environmental protection and human comfort.

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