Prospects for reversible electrodeposited electrochromic devices

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The application of reversible electrodeposition electrochromic technology in the field of smart windows shows great potential for effective management of sunlight and heat by controlling the color and transparency changes of materials through electric fields. However, despite the significant progress in optical modulation amplitude, energy efficiency, and easy preparation of large area devices, the technology still faces some challenges, such as susceptibility to side reactions, absence of an intermediate state, and inability to modulate visible to infrared light independently. In this paper, we look forward to the future development of reversible electrodeposition electrochromic smart windows, and propose that by rationally selecting solvents and endowing the devices with bistable and intermediate states, it is expected to improve its practicability further, and thereby promoting the wide application of electrochromic smart windows in sustainable development.

INTRODUCTION

In the context of the global response to climate warming, dynamic windows based on electrochromic, capable of regulating light transmittance according to the ambient temperature, are necessary, which helps reduce the indoor demand for lighting, heating, cooling and further achieves energy-saving effects and reduces CO_2 emissions. Electrochromism is a phenomenon in which a material experiences a reversible change in its optical properties after gaining or losing electrons. Electrochromic materials such as inorganic oxides, organic small molecules, and conductive polymers are used in various fields, including energy-saving, display technology, and military applications, due to their diversity in color.[1] Nevertheless, they offer no appreciable benefits in terms of price, durability, or optical modulation when used in dynamic windows. Reversible electrodeposition, a method of controlling the deposition or dissolution of metal ions utilizing an external electric field, thereby realizing a reversible adjustment of the optical properties of a material, including metal, metal oxide, and non-metallic monomers electrodeposition, has also been used in large-area electrochromic devices since 2021, with the main application area being dynamic windows.[2] This perspective focuses on the deposition of widely used metal ions, rather than nonmetals.

Specifically, electrochromic devices based on reversible electrodeposition generally contain acid and metal ions in the electrolyte. Taking metal deposition as an example, when the applied voltage reaches the deposition potential of the metal ions, the metal ions migrate to the cathode, where they receive electrons and are reduced to metal, resulting in the coloring of the device. After withdrawing the voltage, the acid in the electrolyte will dissolve the deposits, and applying a lower reverse voltage can further expedite the movement of metal ions, thereby accelerating the dissolution process and ultimately restoring the device to a colorless state. Electrodeposition has long been used in electrochromism, such as for preparing electrochromic polymer films or covalent organic framework films. However, these methods have traditionally focused only on the preparation of color-changing materials. In contrast, reversible electrodeposition, due to its reversible property, allows for continuous deposition and subsequent dissolution, thereby enabling the color-fading process in electrochromism. Moreover, reversible electrodeposition induces color changes exclusively via the processes of ion deposition and stripping, without necessitating ion embedding and stripping. This distinct mechanism confers superior cyclic stability compared to other methods. Metals have a high extinction coefficient, which significantly diminishes the transmittance of the device to approach zero upon deposition, yielding an all-black state. Nevertheless, reversible electrodeposition electrochromic devices still face problems such as electrolyte leakage and the absence of an intermediate state.

CURRENT STATE OF ELECTRODEPOSITION FOR ELECTROCHROMISM

In contrast to commercially available electrochromic devices, the most significant advantages of electrochromic devices based on reversible electrodeposition are low cost and simplified fabrication process, while still enabling the preparation of all-black devices with larger areas. The current price of commercial electrochromic glass exceeds 5000 yuan per square meter, and commonly employed color-changing materials include WO_3 and electrochromic polymers. Although WO_3 is relatively inexpensive, its integration into devices typically requires sputtering, an additional process that contributes to overall fabrication complexity. Electrochromic polymers are synthesized in complicated steps. While metal salts are cheap and easy to obtain, dissolve them in water and then inject into two bonded substrates for encapsulation to obtain electrochromic devices based on reversible electrodeposition.

Researchers prefer to use Cu^{2+} as deposition ions because of its low deposition potential, reversibility, and affordability. One of metal ions like Pb^{+}, Ag^{+}, and Bi^{3+} is added to the electrolyte as a second electrodeposition of metal ion, co-deposit with Cu^{2+}, forming an electrodeposition pair, to improve performance, which results in higher contrast and faster response.[3] However, because of the toxicity of Pb^{+}, the high cost of Ag^{+}, and the high acidity needed to dissolve Bi, researchers have been progressively investigating novel metal ion deposition. Despite the deposition potential of Zn being − 0.76 V, the researchers found that Zn can be deposited prior to hydrogen precipitation when employing the Cu-Zn deposition pair.[4] Metal oxide deposition involves the deposition of Mn^{2+} to produce MnO_2. Although the dissolution mechanism of MnO_2 is still unclear, scientists have found that the compound has several uses except for modulating visible light. These include the creation of electrochromic devices that do not require traditional electrodes, and the ability to modulate ultraviolet (UV) light.

CHALLENGES AND PERSPECTIVE OF REVERSIBLE ELECTRODEPOSITED SMART WINDOWS

While reversibly electrodeposited electrochromic devices offer many significant advantages, their performance as dynamic windows need improvement for large-scale applications (Figure 1).

Water, characterized by its excellent polar solvent properties, is widely employed as the electrolyte solvent in reversible electrodeposition electrochromic devices. However, water has a narrow electrochemical stability window (ESW) and is also prone to irreversible side reactions with metal ions and precipitation of hydrogen gas. Designing or modifying the aqueous electrolyte to modulate the interfacial electrochemical reaction process can broaden its ESW. The implementation of ultrahigh concentration electrolytes, commonly referred to as water-in-salt electrolytes (WiSE), has demonstrated significant potential in expanding the electrochemical stability window of aqueous systems, such as the addition of high-concentration LiTFSI or $LiNO_3$, can broaden ESW of the electrolyte to 2.5 – 4.5 V.[5] Furthermore, the mixing of Lewis acid and Lewis base added to water can form an aqueous eutectic solution, which can reduce the water molecule activity and broaden the ESW. Except for water, researchers have experimented with co-solvents like DMSO and acetonitrile, which can replace water in some devices.[6] This approach not only avoids hydrogen precipitation but also lowers the melting point of DMSO, making it suitable for universal application. When choosing other solvents,

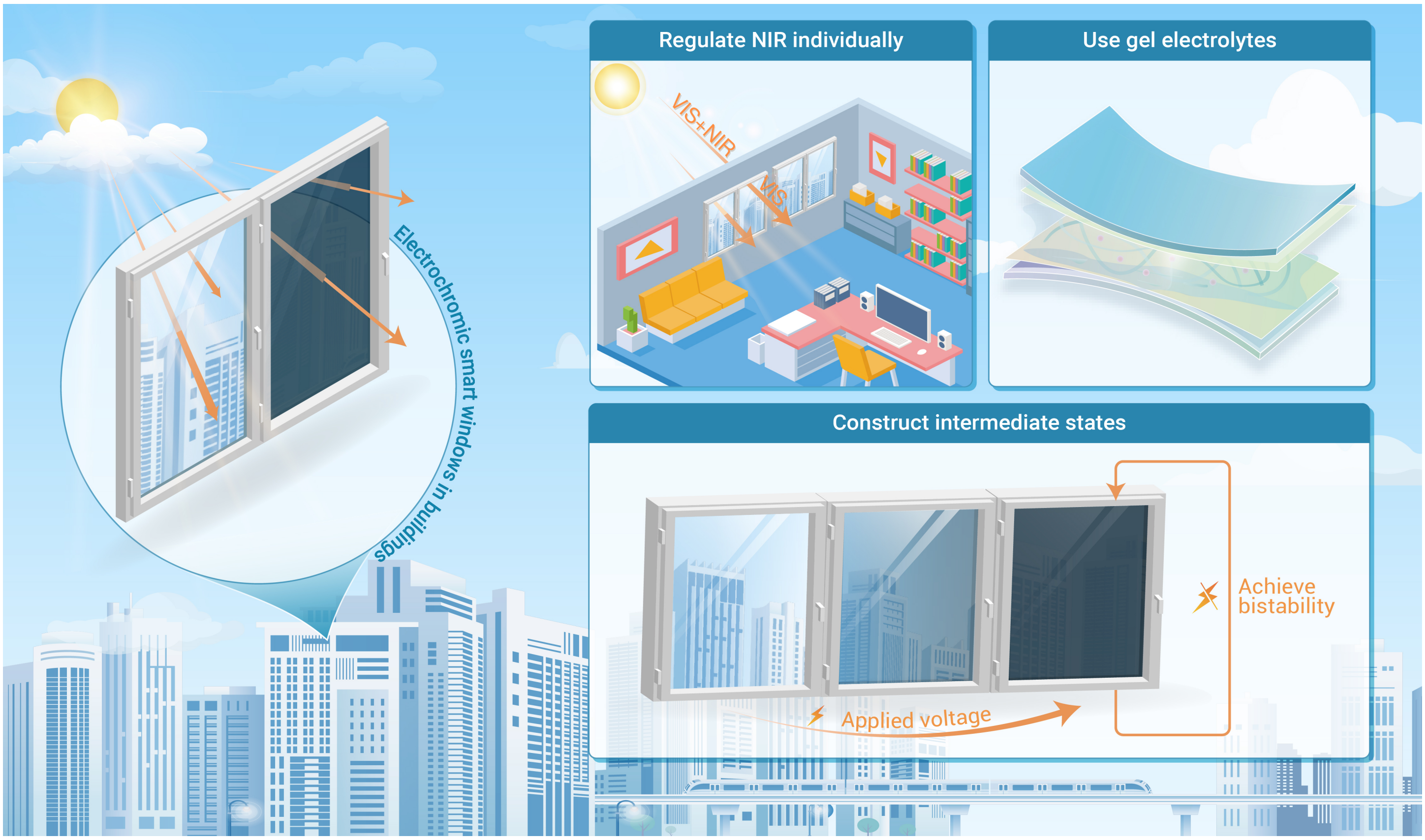

Figure 1. Application of electrochromic smart windows based on reversible electrodeposition in buildings and the direction of development.

high-polarity solvents are preferable. The dissolution process of metal salts depends on the interaction between the solvent and the ions, non-polar solvents lack polar groups, which can't form a stable solvation structure with the metal ions, so the solubility of metal salts in non-polar solvents is generally diminished. The solubility of various metal salts in different polar solvents exhibits significant variation. DMSO and DMF have better solubility for most of the metal halides and nitrates, acetonitrile has a higher solubility for perchlorate, but poorer solubility for halides, and sulfate has a lower solubility in the three solvents. For ionic liquids, the solubility mainly depends on the strength of the anion or cation of the inorganic salt to bind to the ionic liquid. Studies show that some ionic liquids have higher solubility for Lithium bis(trifluoromethanesulphonyl)imide (LiTFSI), ammonium thiocyanate ([NH_4][SCN]), sodium thiocyanate (Na[SCN]), ammonium chloride (NH_4Cl) and other inorganic salts; some hydrophilic ionic liquids have better solubility for cobalt chloride ($CoCl_2$), nickel chloride ($NiCl_2$), copper chloride ($CuCl_2$).[7] When choosing ionic liquids as solvents, the anions with higher polarity should be used as much as possible. For example, the introduction of hydroxyl groups in the cation structure to enhance the hydrogen bonding between the anions; the choice of hexafluorophosphate (PF_6^-) and bis(trifluoromethanesulfonyl) imide ($TFSI^-$) is likely to yield ionic liquids with elevated polarity. Further, to address the issue of electrolyte leakage, substituting a liquid electrolyte with a gel electrolyte represents an effective solution.

Second, metal ions continuously migrate toward the electrode to deposit after the deposition potential is reached. This indicates that the time of applying the voltage has a greater effect on the amount of deposition than the voltage. Consequently, the device can only be in either a bleached state or a fully colored state, with no stable intermediate states available. Researchers combined Prussian blue (PB) with Cu-Zn electrodeposition to realize three different states: a bleached state where no materials were colored, a state where only PB was colored, and a state where both PB, Cu and Zn were deposited.[8] But this device requires voltage to maintain the bleached state, which leads to higher energy consumption. Selection of electrochromic materials that have a low color change voltage and whose degree of coloration is controlled by the voltage, such as conductive polymers like thiophene derivatives, can achieve a stable intermediate state by coloring before the deposition of metal ions. When the voltage is further increased, the metal ions begin to be deposited, and a fully colored state is achieved. This device enables users to adjust the window's transmittance according to their requirements.

When an external electric field causes an electrochromic device to change color, if it can hold onto that color state without an external voltage until the subsequent voltage application, this property is known as bistability and helps to promote "zero-energy-consuming" buildings. For devices colored by reversible deposition of metals, the incorporation of ionic liquids into the electrolyte to form an electrical double layer (EDL) represents an effective strategy to confer bistability upon the device.[9] Under the effect of an electric field, metal ions are reduced and deposited at the cathode, and the negative charges also move to the cathode. To maintain the electroneutrality, the cations in the ionic liquid gather in the cathode to form an adsorption layer, and the anions are located in the diffusion layer of the EDL, which can't be contacted with the deposited metal, delaying the dissolution time of the metal and realizing the stable coloring state. Apart from this, the incorporation of a cationic gel layer in the device structure, which slows down the diffusion of anions into the deposited metal layer, may also achieve a steady state effect. However, the viscosity of the ionic liquid and the thickness of the cationic gel layer will inevitably increase the diffusion resistance for metal ions, thereby prolonging the switching time.

Lastly, apart from visible light, the infrared spectrum contains 47% of the solar energy. It is necessary to improve the current electrodeposition based smart windows since they do not completely control the infrared (IR) spectrum.[10] The traditionally used ITO or FTO glasses absorb infrared light and can not be used to modulate the infrared light, so it is necessary to use a substrate material that meets the requirements, such as polyethylene (PE), poly(methyl methacrylate) (PMMA). Then, combining reversible electrodeposition with IR transmittance-adjustable materials, such as VO_2, enables substantial, independent adjustment of IR and visible light transmittance, and achieves four states: bright, dark, warm, and cool. This makes them more intelligent and better at meeting user needs.

CONCLUSIONS

This perspective focuses on the current status and future directions of reversible electrodeposition in electrochromic smart windows. The materials needed for this device are cheap and the device is simple to prepare, and the device can achieve an almost all-black coloring state. Similarly, the windows still need some improvements before they can hopefully be used on a large scale, making the home intelligent and futuristic. For instance, addresses the primary issue of no intermediate state and the challenge of difficult liquid electrolyte encapsulation through functionalized electrolyte preparation, and designs device structure, while providing bistability, infrared light modulation, and other crucial smart window characteristics.

REFERENCES

1. Xuan Z. Y., Li J. Y., Liu Q. Q., et al. (2021). Artificial structural colors and applications. *The Innovation* **2**:100081. DOI:10.1016/j.xinn.2021.100081
2. Strand M. T., Hernandez T. S., Danner M. G., et al. (2021). Polymer inhibitors enable >900 cm^2 dynamic windows based on reversible metal electrodeposition with high solar modulation. *Nat. Energy* **6**:546–554. DOI:10.1038/s41560-021-00816-7
3. Barile C. J., Slotcavage D. J., Hou J., et al. (2017). Dynamic windows with neutral color, high contrast, and excellent durability using reversible metal electrodeposition. *Joule* **1**:133–145. DOI:10.1016/j.joule.2017.06.001
4. Islam S. M. and Barile C. J. (2021). Dynamic windows using reversible zinc electrodeposition in neutral electrolytes with high opacity and excellent resting stability. *Adv. Energy Mater.* **11**:2100417. DOI:10.1002/aenm.202100417
5. Zheng J., Tan G., Shan P., et al. (2018). Understanding thermodynamic and kinetic contributions in expanding the stability window of aqueous electrolytes. *Chem* **4**:2872–2882. DOI:10.1016/j.chempr.2018.09.004
6. Bhoumik N. C., Madu D. C., Moon C. W., et al. (2024). Nonaqueous electrolytes for reversible zinc electrodeposition for dynamic windows with excellent optical contrast and durability. *Joule* **8**:1036–1049. DOI:10.1016/j.joule.2024.01.023
7. Pereiro A. B., Araújo J. M. M., Oliveira F. S., et al. (2012). Solubility of inorganic salts in pure ionic liquids. *J. Chem. Thermodyn* **55**:29–36. DOI:10.1016/j.jct.2012.06.007
8. Wang L., Jiao X. L., Chen D. R., et al. (2022). A solar water-heating smart window by integration of the water flow system and the electrochromic window based on reversible metal electrodeposition. *Adv. Sci.* **9**:2104121. DOI:10.1002/advs.202104121
9. Yin Y., Zhu H., Wu T., et al. (2022). Bistable silver electrodeposition - based electrochromic device with reversible three - state optical transformation by using WO_3 nanoislands modified ITO electrode. *Adv. Mater. Interfaces* **9**:2102566. DOI:10.1002/admi.202102566
10. Shao Z. W., Huang A. B., Cao C. C., et al. (2024). Tri-band electrochromic smart window for energy savings in buildings. *Nat. Sustain.* **7**:796–803. DOI:10.1038/s41893-024-01349-z

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AUTHOR CONTRIBUTIONS

Baoyi Ma is responsible for data collection and organization as well as the writing of the paper; Xun Cao made changes to the content of the article. All authors contributed to the manuscript and approved the final version.

DECLARATION OF INTERESTS

The authors declare no competing interests.