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Advances in the Study of Gel Polymer Electrolytes in Electrochromic Devices

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Abstract

The electrolytes in electrochromic devices (ECDs) serve as a conduction medium between electrodes and providing compensating ions for electrochromic reactions. Their characteristics directly affect the performance of electrochromic devices. Due to their ease of processing and encapsulation and high ionic conductivity, polymer gel electrolytes are widely used in electrochromic devices. As gel electrolyte polymers, polyethylene oxide (PEO), polymethyl methacrylate (PMMA), and polyvinylidene fluoride (PVDF) are reviewed according to their polymer matrix. Furthermore, future development trends in gel polymer electrolytes are discussed.

Keywords: gel polymers, electrolytes, ionic conductivity, electrochromic devices

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1. Introduction

A reversible color change can be achieved by applying an electric field to an electrochromic device. Due to their relatively low operating voltages, short color change times, and high coloring efficiency, electrochromic devices are widely used in smart windows, displays, smart sunglasses and anti-glare rearview mirrors in automobiles (Fang et al., 2021; Yang et al., 2020; Madasamy et al., 2019; Wang et al., 2019; Rosseinsky & Mortimer, 2001).

Electrochromic devices are commonly constructed as "sandwich" structures (Figure 1).

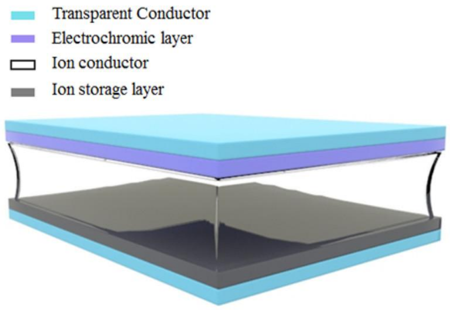

Figure 1. Schematic representation of a typical ECD (Cai et al., 2016)

Transparent conductive layer attached to a substrate surface requires high electrical conductivity and good light transmission.

(Rosseinsky & Mortimer, 2001). The electrochromic layer is the most significant part of the whole electrochromic device. It directly determines the optical performance change of the electrochromic device. The ion storage layer acts primarily as a repository for reverse migrating ions during electrochromic reactions and achieves a charge balance with the electrode.

The electrolyte layer provides and transports ions during an electrochromic reaction, and is therefore also known as the ion conductivity layer. Electrochemical devices require electrolytes that meet the following conditions (Thakur et al., 2012a; Rosseinsky & Mortimer, 2001): (1) high ionic conductivity at ambient temperature; (2) certain mechanical properties; (3) high ion mobility; (4) thermal and electrochemical stability; (5) high optical transparency; (6) good electrode compatibility.

Electrolytes in electrochromic devices are classified into liquid, solid, and gel electrolytes based on their liquid content.

A liquid electrolyte is the most widely studied electrolyte, which has obvious advantages, such as higher ionic conductivity and greater optical transmittance due to the mobility of free solvent to drive ionic conduction, and has a wide range of applications in the field of batteries. To investigate the performance of prepared electrochromic materials, liquid electrolytes are often used as the electrolyte layer. This is to test the performance of the devices. This can ensure the rapid color change of electrochromic materials and minimize the influence of the electrolyte layer on the device transmittance. The application of liquid electrolytes to electrochromic devices, however, has significant disadvantages, including corrosion resistance, chemical stability, low resistance to harsh environments, and difficulty in encapsulating. In particular, the electrolyte cannot be formed into thin films, making it unsuitable for electronic devices with small volumes, light masses, high specific energy, and long life cycles (Au & Chan, 2022).

Solid-state electrolytes are electrolytes in which the percentage of liquid mass in the electrolyte system is less than 25% and the solvent is not present in the form of free molecules. As a result of the absence of free solvent molecules in solid-state electrolytes, ions can be transported primarily by rearrangement of flexible chain segments in the polymer substrate. In addition, the small amount of solvent present in it coordinates with Li+ and facilitates chain segment movement by using the plasticization effect. Generally, all-solid electrolytes are prepared by melting polymer frameworks and blending them with lithium salts, and then cooling them. Due to their inherent characteristics of high mechanical strength, safety, and reliability, these electrolytes make the most suitable electrolytes for flexible electrochromic devices. Furthermore, they can be commercialized by using simple raw materials and continuous preparation, making them ideal for the commercialization of flexible electrochromic devices. The ionic conductivity of solid electrolytes still lags behind that of liquid electrolytes, and improving the ionic conductivity of solid electrolytes will be a major goal of future research (Shao et al., 2022; Au & Chan, 2022).

An electrolyte containing a percentage of liquid solvent mass of approximately 50% is referred to as a gel state electrolyte. Gel electrolytes have a higher ionic conductivity than solid electrolytes and all-solid electrolytes, and their ionic conductivity is around 10^{-3} S/cm at room temperature. Due to the large volume of liquid present, ion pairs can easily dissociate, thus improving ion transport efficiency. Gel polymer electrolytes are composed of polymer matrix, organic plasticizer, and lithium salt. The polymer matrix ensures sufficient mechanical strength, while the organic plasticizer and lithium salt provide the path for lithium ion transport. The main substrates used for gel polymers in electrochromic devices are PEO, PMMA, and PVDF (Thakur et al., 2012b; Pu & Huang, 2005; Ding et al., 2022).

In this paper, we summarize the research progress on gel polymer electrolytes in electrochromic devices in recent years, and emphasize the relationship between polymer matrix structure and properties. The final part of this thesis presents an outlook on the development of gel polymer electrolytes in order to promote the development and application of electrochromic devices with high performance.

2. PEO/PEG Based Polymer Electrolytes

Since Armand proposed PEO-based electrolytes for lithium-ion batteries in 1978, research in this area has become increasingly extensive (Su et al., 1997; Su et al., 1998; Honma, Hirakawa & Bae, 1999; Zhang et al., 1999; Honma, Takeda & Bae, 1999; Honma, Hirakawa, Yamada et al., 1999; Rodrigues et al., 2011) (Kanao et al., 2020a). It offers many advantages, including high safety, simplicity of manufacture, low cost, good electrochemical stability, and compatibility with lithium metal anode and lithium salt. When lithium salt is mixed with PEO, there are three phase regions in the polymer electrolyte at normal temperature: pure PEO phase region, amorphous phase region and salt-rich phase region. The ion transport occurs primarily in the soft amorphous region of the chain segment. In the amorphous region, the lithium salt dissolved in PEO matrix interacts with the ethylene oxide group (-CH2CH2O-) to form a stable complex. Ion migration is realized by lithium ions complexing-dissociating through the movement of polymer chain segments. Most of the chain segments of the crystallized part are frozen, and the movement ability is very limited, resulting in the conduction of lithium ions being blocked. Typical ionic conductivity at room temperature is 10^{-8}-10^{-4} S/cm, which limits its application in electrochromic devices. It is generally necessary to modify PEO in order to improve ionic conductivity at room temperature. By blending(Barbosa et al., 2010) (Alamer et al., 2015), copolymerizing (Cots et al., 2021) and crosslinking (Gong et al., 2008), PEO matrix was modified to reduce the crystal zone, increase the chain segment kinematics, enhance lithium salt dissociation, and improve its ionic conductivity.

Guan S et al. prepared a polymer electrolyte using modified PMMA-PEG polymer loaded with LiClO4/PC, which exhibits a high conductivity (5.23 x10^{-6} S/cm at room temperature).(Guan et al., 2020) Wang W et al. developed a hybrid quasi-solid polymer electrolyte (QSPE) by mixing mPEG prepolymer with porous PVB. The prepared QSPE exhibits high ionic conductivity at the level of 10^{-5} S/cm and good luminous clarity (light transmittance of at least 70% in the visible light region). (Wang et al., 2018)

Gong Y et al. synthesized a star network polymer, composed of four PEG-block polymeric arms linked by a pentaerythritol core. Using $LiClO_4$ and EC/PC, gel polymer electrolytes showed thermal stability up to 150 degrees C and ionic conductivity up to 8.83 x 10^{-4} S/cm at room temperature (Gong et al., 2008).

Zhu Y modified PEG to produce poly(ethylene glycol) dimethacrylate (PEGDMA) and poly(ethylene glycol) methacrylate (PEGMA), adding lithium trifluoromethanesulfonate (LiTRIF) and propylene carbonate (PC) in order to produce a gel electrolyte with a conductivity of 1.36 x 10^{-3} S/cm. (Zhu et al., 2014).

Similarly, Zheng P et al. prepared quasi-solid polymer electrolytes in a gel state by UV cross-linking PEGMA and PEGDA, then enclosing PC and $LiClO_4$ within the polymer structure. In thin film state electrolytes formed with PEGMA/PEGDA monomer ratios of 75/25 and lithium salt solution percentages of 75%, there was 14 times higher ionic conductivity than that of the original solution. After applying electrolyte to the electrochromic device, the device still achieved stable and fast color switching, with both colors changing within 3 seconds. (Zheng et al., 2021) The ionic conductivity of polymer electrolytes increased with the addition of dimethylacetamide (DMA) as a plasticizer. Kumar R et al. obtained polymer electrolytes by complexing HCF_3SO_3 with PEO. It was found that the plasticized polymer electrolyte had an increased ionic conductivity (8.14 x 10^{-3} S/cm) after the addition of nano-sized SiO_2.(Kumar et al., 2017)

3. PMMA Based Polymer Electrolytes

PMMA consists of an amorphous phase and a flexible backbone with high ionic conductivity, which has received a lot of attention in electrochromic applications (Kanao et al., 2020b; Theodosiou et al., 2019; Zhang, Hu et al., 2019; Hsiao et al., 2019; Zhang, Chen et al., 2019; Padmaraj et al., 2016; Kumar, 2015; Mihelcic et al., 2014). In addition to being rich in polar carbonyl groups, PMMA is compatible with both ester and ether electrolytes, has a high affinity for lithium ions, thereby making it an excellent polymer for forming complexes between inorganic salts and polymers (Tung & Ho, 2006). Moreover, PMMA is highly transparent, has good environmental stability, abundant raw materials, is inexpensive and easy to prepare, and is non-toxic and non-fluorinated, which are of particular interest in electrochromic applications (Vasilopoulou et al., 2006; Deepa et al., 2002). The problem with PMMA is its poor mechanical properties and brittle matrix, which prevents it from being used as an electrolyte film alone. To overcome these limitations, multiple substrates and doped nanoparticles should be mixed together (Kim et al., 2019) (Wang et al.,

2017) or cross-linked with PMMA (Li et al., 2020) (Lee et al., 2020).

TiO_2 and ZnO fillers improve the physical and electrochemical properties of PMMA gel electrolyte by acting synergistically. (Pullanjiot & Swaminathan, 2019) Kuo et al. fabricated a SiO_2 nano-hybrid polymer electrolyte with PMMA as a matrix and measured its ionic conductivity to be 1.57×10^{-3} S/cm. Hybrid polymer electrolytes were inserted into polyaniline-polystyrene sulfonic acid (PANI-PSS) and poly3, 4-vinyl dioxyethiophen-polystyrene sulfonic acid (PEDOT-PSS) to form devices with good optical and electrochemical properties and faster discoloration response time than without SiO_2. (Kuo et al., 2014)

According to Khan S et al., composite GPE with core-shell structured SiO_2-PMMA and PVDF-HFP polymer matrix showed high light transmission, good thermal stability and the highest ionic conductivity of 2.22×10^{-3} S/cm for 10% doping. (Khan et al., 2021) According to Tang Q et al., the ionic conductivity of PMMA-based gel electrolytes doped with [Emim]BF4 reached 2.9×10^{-3} S/cm at room temperature. Furthermore, [Emim]BF4 reduced the anodic reaction potential in ECD, allowing it to be bleached at a lower voltage and preventing ion capture in tungsten oxide (W0(3)) films that resulted in degradation of light modulation. (Tang et al., 2017)

4. PVDF Based Polymer Electrolytes

A strong electron-absorbing group fluorine atom (C-F) is present at the main chain of PVDF, which contributes to the dissolution of lithium salts and improves its ionic conductivity. The high dielectric constant of 8.4 contributes to the dissolution of lithium salts, which possess a strong polarity to improve swelling in organic solvents (Idris et al., 2012). The PVDF material exhibits good plasticity, mechanical strength, electrochemical stability, and thermochemical stability, making it suitable for use in electrolytes. As PVDF is ineffective for polymer-salt complexation, the introduction of HFP enhances the mechanical properties of the copolymer while maintaining a high electrical conductivity by encapsulating the liquid electrolyte and crystalline part (Fabretto et al., 2008). In the poly (vinylidene fluoride-co-hexafluoro-propylene) (PVdF-HFP) and PVDF-HFP-based electrolyte system, PVDF-HFP contains an amorphous domain (HFP) that traps a large amount of liquid electrolyte, as well as crystalline regions (VDF) which provide chemical stability with sufficient mechanical integrity, eliminating the need for crosslinking treatment. In order to improve the conductivity of PVDF-HFP-based electrolyte systems, inorganic nanoparticles such as SiO_2 and TiO_2 can be doped in combination with other polymer matrixes in order to increase the structure of the polymer network. Puguan J M C et al. doped ZrO2 nanoparticles in the PCDF-HP system with greatly improved performance. (Puguan et al., 2016; Puguan et al., 2015)

Guan S et al. fabricated PVDF-HFP nanocomposite polymer electrolytes using NH_4F salt, dimethylformamide plasticizer, and Al2O3 filler. The polymer electrolyte demonstrated an increase in ionic conductivity from 10^{-7} to 10^{-3} S/cm, as well as a significant increase in conductivity by three or four times. During the 30-130 degree Celsius range, the conductivity remains constant. (Sharma et al., 2017)

5. Conclusion and Future Outlook

Among the next generation of high-performance electrolytes, polymer gel electrolytes, which combine the advantages of easy processing and packaging of solid electrolytes with high ionic conductivity of liquid electrolytes, have received considerable attention in the past few years. Polymer gel electrolytes are most likely to replace organic electrolytes in the future. This paper reviews the research progress of gel polymer electrolytes in electrochromic devices and discusses the advantages and disadvantages of gel electrolytes based on various polymer matrices, respectively. The use of copolymerization, cross-linking, blending, pore formation, double networks, and inorganic ion doping has greatly improved the performance of gel polymers.

An electrochromic device requires gel electrolytes to have high ionic conductivity, certain mechanical properties, acceptable ionic mobility, good thermal and electrochemical stability, high transmittance, and good compatibility with electrodes. There is a reciprocal relationship between these requirements. As an example, the introduction of plasticizers into polymer electrolytes can significantly increase the ionic conductivity of the gel electrolyte by reducing the crystallinity of the polymer matrix, but at the same time, the mechanical strength of the electrolyte will be significantly diminished. As a result of the poor mechanical properties and the high viscosity of the gel, ECD processing is inconvenient. It may also lead to short circuits inside the devices, thereby reducing their service life and posing safety concerns.

Therefore, future research on gel polymer electrolytes needs to establish a good balance among the properties, and the main directions of reference are as follows: a) Develop and synthesize new polymers for polymer electrolyte systems; b) Develop new polymer networks through chemical or radiation cross-linking, in order to improve the performance of polymer electrolytes; c) The use of additives and fillers is an effective method for improving the performance of gel polymer electrolytes, and further study of the interaction between these additives and the polymer matrix will contribute to the development of new electrolytes.

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