

Application of quasi solid electrolytes in organic based electrochromic devices: A mini review

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The interest in all solid organic based electrochromic devices (ECDs) is on the increase. This is because these devices offer the applicability of electrochromic materials in products such as smart sensors, smart windows, flexible wearables and energy storage devices. The use of quasi-solid electrolytes for the construction of these ECDs is attractive because of their ease of preparation, availability, low cost, improve electrochromic performance, good ionic conductivity and prevention of leakages in ECDs. Hence, in this review, a detailed discussion is presented on the progress in the development of semi-solid

electrolytes for ECDs fabrication. The preparation of the most common electrolytes that have been applied for organic based ECDs are summarized. Particular attention is given to efforts and strategies that have been adopted to improve the efficiency of quasi-solid electrolytes. Importantly, knowledge gaps that warrant further research are clearly identified and recommendations for future works are suggested. This review will be very beneficial for both established and new researchers in the field of electrochromic devices and material science.

1. Introduction

Giant strides have been seen in the world of smart technology for better quality of life. The progress that has been made in the development of electronic devices has been significant, with their applications spanning many different areas. With the application of any electronic device is of course largely dictated by the materials employed in its fabrication, this is always the first consideration that should be made for any new material. An outstanding class of materials are the electrochromic materials which are finding applications in supercapacitors, smart windows, sensors, flexible electronic devices, electronic papers and energy storage devices.^[1–6] Materials that exhibit stable and reversible changes in optical properties (or colour) when subjected to external potential are termed electrochromic materials.^[7] The discovery of electrochromic materials has been a game changer in the generation of alternate source of energy in that this materials are capable of harnessing solar energy for numerous applications. Hence, extensive attention has been directed to the development and deployment of efficient electrochromic materials. Based on the nature of materials, electrochromic materials can be classified as inorganic and organic materials. In the inorganic electrochromic materials, electrochromism originates from the presence of mixed redox state of the metallic centre with tungsten trioxide remaining the most studied inorganic electrochromic material.^[8,9] Conversely, electrochromism in organic materials originates from their highly conjugated systems. Prominent examples include

quinones, conductive polymers and viologens.^[10–12] For practical applications, these materials are integrated with other constituents for electrochromic devices (ECDs).

Generally, an ECD is similar to a thin film battery with the ability to display different colour change subject to the charged and discharged state of the battery. A typical ECD consists of seven distinct layers.^[13,14] The working electrode is comprised of a conducting substrate, conducting thin film and the electrochromic materials. The counter electrode, on the other hand, has the conducting substrate layer, conducting film and an ion storage layer. Since two couples must be involved in between the two electrodes, there is another layer is the one separating the conducting electrode from the counter electrode, and this is usually an ionic conductor layer (electrolyte). The electrolyte layer can be ionic liquid, gel or solid in nature. However, the most practical setup for commercializing ECDs involves the use of a solid or semi-solid electrolyte to prevent leakage or drying on the device. As stated earlier, the nature of the electrochromic materials in an ECD determines its properties, but the nature of electrolyte use is also critical. This is because the electrolyte determines the ionic conduction between the working electrode and the counter electrode. Therefore, it is expected that a typical electrolyte possesses some inherent properties which include sufficient ion conductivity, good transparency in the spectrum region and being confined to enable easy determination of specific surface area of ECD. Consequently, gel and solid electrolyte offers better practicability than liquid electrolyte.

As a result of extensive research on electrochromic materials, a number of review articles have been published.^[15–19] However, the majority of these reviews focus primarily on the nature of electrochromic materials. For example, Madasamy *et al.* compiled a review on the application of viologen based electrochromic materials where a detailed discussion on the synthesis of viologen-based organic and inorganic electrochromic materials, their modifications and the fabrication of

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ECDs was presented.^[15] In another review article, the preparation and application of polymer-based electrochromic materials has been summarized by Wang *et al.* In this review article, the authors highlighted several strategies employed for the synthesis of conjugated polymer based ECDs.^[16] Additionally, they presented a critical discussion on the whole construction of the polymer-based ECDs and particular attention was given to the appropriate preparation and application of sealants in ECDs construction. Other similar reviews on the application of polymer-based ECDs include the those written by Neo *et al.*^[17] and Jensen *et al.*^[18] Understanding the crucial role of electrolytes in the fabrication of ECDs, researchers have also written review articles on the applications of several kinds of electrolytes for ECDs. For example, Yang *et al.* have discussed the applications of polymerized ionic liquids as suitable electrolytes for ECDs.^[20] Also, Thakur *et al.* have also presented a concise discussion on the applications of polymer electrolytes in functional ECDs.^[19] Notably, these reviews pay larger attention to the applications of liquid electrolytes in ECDs. However, solid or semi-solid electrolytes are particularly desirable for ECDs and recent studies on ECDs have focused on the use of quasi-solid or solid electrolytes due to the practicality in real world devices. In a report by Azarian and Woottikanokkhan, a summary on the use of gelatin-based solid electrolytes for ECDs was presented.^[21] However, it is necessary to evaluate the recent progress in the use of different kinds of quasi-solid electrolytes for ECDs especially with the progress in the chromic materials themselves, especially with organic based ECD.

Therefore, in this present review, a summary on the applications of quasi-solid and solid electrolytes is presented. Firstly, a concise discussion on the mechanism and design of ECD is presented. Additionally, the salient properties of common quasi-solid electrolytes are summarized and discussion on the synthesis of the solid electrolytes and their applications in ECDs. This review will provide researchers with an up-to-date progress report on the methods adopted for ECDs solid electrolytes and help them to make informed decision when it comes to selection of materials and design of effective ECDs.



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2. An overview of Electrochromic Devices (ECDs)

The major components of a typical ECD are shown in Figure 1. An efficient ECD consists of an electrochromic material that easily changes colour in a reversible manner due to redox reaction originating from the passage of electron. The colour change of the electrochromic material could be from a bleached state to a coloured state or from one colour to a different colour. The electrochromic materials can also be described as either Type I, Type II or Type III based on their physical state at room temperature.^[22,23] For the Type I materials, they are soluble and remain in the solution during application with molecular dyes being typical examples. On the other hand, Type II materials are soluble in their neutral condition but after electron transfer, they become solid on the surface of the electrode. In the case of Type III materials, they exist as solid and remain as solid even after redox reaction. Metal oxide films and conjugated polymers are common examples of Type III materials. In terms of application, Type III materials offers better processability and have found applications. Moreover, conjugated polymers which have relatively low cost have been found to exhibit impressive response times, intense colour versatility, low energy consumption with good optical contrasts.^[24] More desirable is the fact that these properties can easily be improved through structural control and facile preparation. However, for solid ECDs, classification of electrochromic materials based on their colour change is more fitting. Accordingly, the electrochromic materials fall into two broad categories: those that change from bleached state to coloured state (Type 1) and those that change from a coloured state to another coloured state without having any bleached state (Type 2).^[25]

Another major component of the ECD is the conducting substrate which is usually a transparent conducting oxide deposited on a glass and they are employed as the electrodes. Usually, the electrochromic materials can be deposited onto the substrates through spin coating, blade coating, spray coating or electrodeposition.^[26,27] Commonly used substrates include indium doped tin oxide (ITO), fluorine doped tin oxide (FTO) and aluminum doped zinc oxide (AZO). These substrates offer good



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Figure 1. Major components of an ECD (Adapted from reference).^[16]

optical transparency. Among them, ITO has the highest electrical conductivity.^[28] However, FTO and AZO have gained much popularity due to the scarcity of ITO. These glass substrates are excellent materials when making ECDs for smart windows and mirrors as they are highly transmissive. Though the process of depositing the metal oxides on the glass to form the conducting substrate is cumbersome and expensive, the major limitation of the glass substrates is their brittleness which make them not suitable for paper-like and wearable devices. The need for flexible ECDs have led to the investigation and development of new materials for electrode materials. Prominent materials that have been studied include carbon nano-materials, including nanotubes and graphene.^[29,30] Some outstanding properties of these materials include excellent electrical conductivity, good thermal and chemical stability and they have shown high colour contrast, fast response and good reproducibility when employed for ECDs. In some studies, conducting polymers such as poly (3,4-ethylenedioxythiophene) (PEDOT) and PEDOT doped poly (styrenesulfonate) (PEDOT:PSS)

have been coupled with carbon materials to form electrodes for flexible ECDs.^[31,32] Other materials that have been employed as electrodes include metal nanowire such as silver grids.^[33]

The other major component of an ECD is the electrolyte. The electrolyte provides the necessary ions to enable reaction between the electrodes. The electrolyte is expected to possess some unique chemical and physical properties to ensure effective redox reaction involving the electrochromic materials. Importantly for ECD, the electrolytes should be transparent, chemical and electrochemically stable. The efficiency of the ECD largely depends on the ionic conductivity of the electrolyte. Electrolytes commonly used in ECDs could either be in liquid, solid or semi-solid (Quasi solid) states. Table 1 summarizes some key advantages and disadvantages of each state. Traditionally, the electrolyte consists of solid salts dissolved in an appropriate solvent. It is expected that the electrolyte should have high ionic conductivity and liquid electrolytes have exhibited good ionic conductivity. However, the injection of the liquid into the ECD is technical to prevent the entrapment of

Table 1. Comparison between different states of electrolytes used in ECDs.

Electrolyte states	Advantages	Disadvantages
Liquid	High ionic conductivity. Good optical transparency. Fast switching times. ^[20]	Difficult to process. Problem of leakages during use. Not ideal for some ECDs including flexible ECDs. Lower chemical stability. Presence of bubbles. Hazards from the organic solvent used. ^[16,38,39]
Solid	Easy to handle. No risk of leakages that could impede ECD performance and also pose environmental risk. Excellent confinement property. ^[19,38]	Low ionic conductivity. Slow switching time Less optical transparency. ^[19]
Quasi-solid	High ionic conductivity compared to solid electrolyte. Good optical transparency. Easy processing Better mechanical stability than liquid electrolytes. Good flexibility, making them suitable for flexible ECDs. ^[39,40]	Slow switching time compared to liquid electrolyte. Lesser ionic conductivities than some liquid electrolytes. Poorer mechanical strength than solid electrolytes. ^[19]

gas within the ECD which could impede the redox reaction. The use of ionic liquid electrolytes in ECD construction often necessitates the use of suitable edge sealants to prevent the leakages of the electrolytes. The sealant will be in direct contact with the two electrodes and the electrolytes. Hence, it is expected that the sealant should be chemically inert, possess good bonding to glass substrate and have low permeability for oxygen and moisture. Examples of sealants that have fulfilled these requirements include epoxy resins, acrylic resins, VHB tapes and polyisobutylene sealant.^[34,35] To overcome the issues related to traditional liquid electrolyte such as stability and conductivity limitations, many studies have used polymerized ionic liquids as electrolytes. These electrolytes have better mechanical properties than liquid electrolytes. Common examples of polymerized ionic liquids include polyethylene, polyoxyethylene, and polyacrylate ionic liquids.^[20,36,37] Though outstanding success has been reported with use of polymerized ionic liquids, their use is limited by their complex preparation route and high costs. In the following sections, discussion on the preparation and application of solid and semi-solid electrolyte is presented.

3. Quasi-solid electrolytes in ECDs

Quasi-solid or semi-solid electrolytes which could be inorganic or polymeric materials in ECDs offer many advantages over liquid electrolytes. Particularly, semi-solid electrolytes based on polymeric materials are fascinating because of their ease of preparation, compatibility and availability. Since some of the polymers used are from natural origin, semi-solid polymeric ECD electrolytes, they are relatively cheap. In order for any material to be viable to be produced commercially, cost and availability of the material is the major priority. Herein, the detailed preparation, mechanism, merits of semi-solid ECD electrolytes based on poly methyl methacrylate, polyacrylamide, poly [(vinylidene fluoride)-co-hexafluoropropylene] (PVDF-HFP) and polyaniline will be discussed. These electrolytes are representative of water-soluble polymers (PAM) and those soluble in organic solvents (PMMA, PVDF).

3.1. Poly (methyl methacrylate) (PMMA) based electrolyte

Among the several kinds of polymers commonly used as solid or gel electrolytes are the poly(acrylates). Their use is very attractive for ECD fabrication because they possess remarkable mechanical strength, outstanding resistance to UV radiation exposure, good thermal stability, impressive film-forming ability and good availability. Additionally, PMMA has exhibited impressive weather resistant properties for outdoor applications.^[41] These qualities can also easily be improved through the formation of composite with suitable materials. Considering the reports on the solid state ECD where poly(acrylates) are used, PMMA is the most commonly used in this class. In many studies, commercially sourced PMMA is used, and suitable ions are incorporated into the polymer backbone to promote conductiv-

ity. A typical electrolyte involves the mixing of PMMA, lithium perchlorate (LiClO_4), propylene carbonate and acetonitrile. For example, Halder *et al.* reported the use of such PMMA based electrolyte for ECD developed using water soluble sulfonate containing arylene diimides as the electrochromic material.^[42] The preparation of the electrolyte was straightforward, and carried out at room temperature with no heating requirement. For the ECD setup, the electrochromic material was drop-cast on ITO glass and this was followed by the spreading of the PMMA gel electrolyte on the same ITO glass. After this, another ITO glass was added to sandwich the gel coated electrochromic film and then heated at 60°C for 1 h. It should be noted that in this study, no additional layer for ion storage purpose was used. The solid ECD achieved a fast colour change which was consistent with the behaviour of the electrochromic material in a liquid electrolyte. This study proved that PMMA is a good candidate to use for the development of semi-solid electrolyte for organic electrochromic materials such as naphthalene diimide electrochromic materials. In a similar study, PMMA gel electrolyte was used to fabricate an ECD device based on iron supramolecular polymer containing thiazolothiazole spacer as an electron withdrawing entity.^[43] The other constituents of the gel electrolyte were also LiClO_4 , PC and acetonitrile. The colour change observed using the electrochromic film in ECD with gel electrolyte was consistent to the colour change noted using the film in liquid electrolyte. Though, the switching time recorded in liquid electrolyte was faster than that of the solid electrolyte, the use of the PMMA gel in the ECD fostered the durability and reusability of the electrochromic material which suggests prospect for real-life applications.

Efforts have been made to further improve the performance of PMMA for semi-solid ECD fabrication. A strategy has been developed is to functionalize the gel electrolyte with an anodic active species and this could significantly increase the conductivity of the electrolyte.^[44] For example, p-benzoquinone (p-BQ) has been added to the PMMA gel electrolyte to improve the performance of iron based metallo-supramolecular polymer (Fe(II)-MEPE) as reported by Xu *et al.*^[45] The gel electrolyte containing p-BQ and the ECD was prepared according to the scheme shown in Figure 2.

Firstly, PMMA, PC and tetrabutylammonium hexafluorophosphate (TBAP) were mixed at 80°C to form the PMMA based gel. Thereafter, specific amounts of p-BQ were added to the gel and further stirred at 40°C to obtain the p-BQ modified PMMA gel electrolyte (GET-BQ). The amounts of p-BQ added was also optimized to understand the effect on the conductivity of the gel electrolyte. As anticipated, the GET-BQ electrolyte showed better conductivity than the GET electrolyte without p-BQ which was confirmed through electrochemical impedance spectroscopy (EIS) shown in Figure 3. However, no obvious difference in conductivity was recorded with the change in the amount of p-BQ added. Introduction of p-BQ into the PMMA gel electrolyte did not only increase the conductivity of the electrolyte but as increase the performance of the Fe(II)-MEPE based ECD. Specifically, a lower driving voltage (-1.1 V) was noted with the use of the GET-BQ electrolyte as compared to the electrolyte without BQ. Additionally, faster colouration

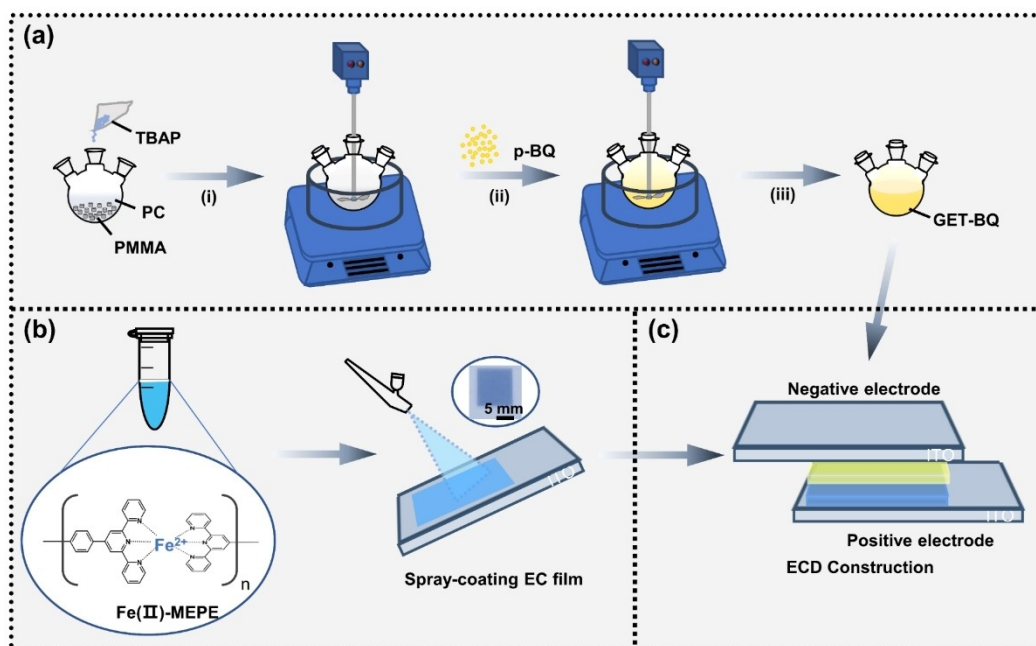


Figure 2. Schematic illustration: (a) the fabrication process of gel electrolyte containing mixed-state *p*-BQ. (b) spray-coating of Fe(II)-MEPE film and (c) assembling of sandwich structure ECD. (Reproduced with permission from reference.^[45] Copyright right Elsevier 2023).

responses and enhanced stability were observed. Hence, the incorporation of cathodic active species such as *p*-BQ into PMMA electrolyte is an appropriate strategy to prepare semi-solid electrolyte with enhanced performance for ECD fabrication. Other compounds that have been added to PMMA electrolyte for better efficiency include ionosilicas such as lanthanide doped ionosilica.^[46] The lanthanide doped ionosilica modified PMMA electrolyte showed higher ionic conductivity than pure PMMA electrolyte. Additionally, doping the PMMA electrolyte also significantly prevents its photo-degradation.

Nevertheless, a major problem that could impede the conductivity of electrolytes containing PMMA is the occurrence of chain entanglements in PMMA molecules and these could

restrict the free mobility of ions. Addition of appropriate compound could overcome this issue. For example, in another study by Zhou et al., succinonitrile (SN) was used improve PMMA gel electrolyte for quasi-solid-state ECD.^[47] The amount of SN in the gel electrolyte was varied relative to that of PC. The conductivities of the prepared gel electrolytes were measured using EIS and the result obtained showed that SN significantly increased the conductivity of the gel electrolyte, and the increase was directly proportion to the increase in the amount of SN added to the PMMA gel electrolyte. The increase in the ionic conductivity was attributed to the role the plastic crystals of SN played in suppressing the entanglements of PMMA chains and this promoted the mobility of lithium ions. Also, it was

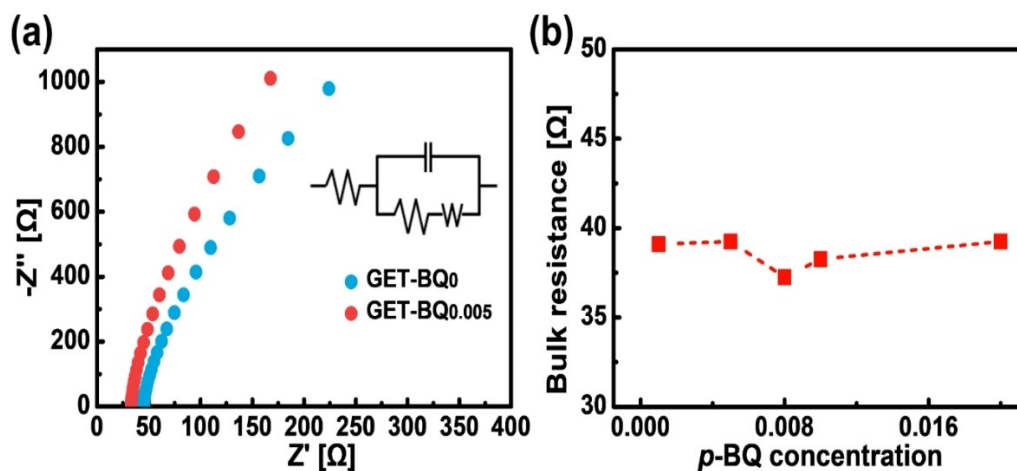


Figure 3. (a) EIS study (Nyquist plot) of gel electrolytes in the range of 1 to 10⁵ Hz. (b) The bulk resistance of GET-BQ with different ratios of *p*-BQ. (Reproduced with permission from reference.^[45] Copyright Elsevier 2023).

observed that the addition of SN into the PMMA gel did not compromise its transparency which made the composite gel ideal for ECD. The better performance of the SN modified PMMA gel electrolyte was not surprising because SN have been identified to be a distinct functional filler due to its molecular plastic crystals which permits it to show short range crystal rotation and orientation disorder while it still maintaining a long-range ordering of crystal lattice.^[48] More so, ECDs fabricated with SN incorporated PMMA gel electrolytes have been found to possess outstanding stability even after several thousands of cycles.^[49]

Another challenge limiting the performance of PMMA gel electrolyte is the limited interfacial adhesion between the electrode and the electrolyte which could result in less stability and reusability due to peeling of the electrolyte. To overcome this, a suitable polymer with enhanced adhesive power could be incorporated into the PMMA electrolyte matrix. For example, polyvinyl butyral (PVB) has been employed to promote the stability and conductivity of PMMA based electrolytes.^[50] The PVB fiber was firstly prepared through electro-spinning and the PMMA precursor electrolyte matrix was coated on the surface of the PVB while free radical polymerization was initiated through UV irradiation. From the results obtained, the presence of PVB in the quasi-solid electrolyte significantly increased the interfacial bonding ability of the electrolyte to the electrode. Specifically, the tensile strength was found to increase from 0.05 MPa to 0.31 MPa. The PMMA electrolyte on PVB template also showed higher ionic conductivity and better stability than the electrolyte without PVB. Importantly too, the transparency of the PMMA gel (over 80% transmittance) did not experience any significant change upon the addition of the PVB. It is also worth noting that the method employed for the preparation PMMA gel, UV curing, is advantageous in that it requires less preparation time. This method was similarly employed for the ECD fabricated by Lee *et al.*^[51] Also, when commercial PMMA is used, the viscosity of the gel is usually difficult to control while in the UV curing process, the in-situ polymerisation overcomes the change of handling the gel. Moreover, UV curing is less energy intensive than heat curing.

Overall, the results reported on the use of PMMA semi-solid electrolyte in ECD fabrication suggest the potential of developing commercialized devices such as smart windows and flexible wearables using the PMMA based electrolyte. Many efforts have been made to overcome many of the drawbacks associated with the use of these electrolytes. Nevertheless, the use of PMMA based electrolytes still calls for further studies such as upscaling the prototype ECDs.

3.2. Polyacrylamide based electrolyte

Polyacrylamide (PAM) is another common quasi state electrolyte that has found extensive application for electronic devices. PAM is a typical water-soluble polymer with good transparency, biocompatibility, excellent mechanical strength, plasticity and high ionic conductivity.^[52,53] The use of PAM in electrochemical systems is attractive because it eliminates the use of organic

solvents (such as PC) for dissolution since it is highly hydrophilic. Additionally, it can easily form hydrogen bonds with other compatible molecules due to the presence of amide group and this often results in higher conductivity. PAM gel electrolytes have been extensively applied in energy storage devices particularly in zinc aqueous batteries.^[54–56] Despite the fascinating properties of PAM as a suitable gel electrolyte for the fabrication of all-solid ECD, only limited reports are available on its use in ECDs.

The preparation of PAM gel which usually involves the use of acrylamide monomer, a cross-linker and polymer initiator is simple, direct and not time consuming. For example, as described by Cai *et al.*, the PAM gel was synthesized by mixing acrylamide monomer, N, N-methylenebisacrylamide cross-linker and potassium persulfate initiator.^[57] The mixture was sonicated and the gel was formed by stirring the mixture at 60 °C for 2 hours. The amount of the cross-linker and initiator were kept constant at 0.046 and 0.13 mol% of the acrylamide monomer respectively. Efforts were also made to optimize the polymerization process by varying the amount of acrylamide monomer from 0.5 to 5 g. The prepared PAM gel was then employed for the construction of an ECD with tungsten trioxide and Prussian blue. A typical schematic diagram of the synthesis process and construction of the ECD is shown Figure 4.

The results showed that the use of 0.5 g and 5 g of the monomer resulted in incomplete polymerization and inhomogeneous gel respectively, which were unsuitable. The conductivity and thermal stability of the other PAM gels (1–4 g of monomer) were further examined. As shown in Figures 5, the EIS revealed that the conductivity of the gel decreased with increase in the quantity of acrylamide monomer used. The decline in the conductivity was attributed to reduction in the water present in the gel. Furthermore, the results from the thermal stability revealed that the degradation of the gel occurred at three temperatures of 100, 280 and 370 °C which are associated with the loss of water molecules, condensation of amide to imide and decomposition of amide to carbon dioxide and nitrogen oxides respectively. Importantly though, the PAM gel satisfies the requirements for ECD applications. The ECD constructed with the prepared gel showed remarkable stability over 13,500 cycles and fast colour response due to high ionic conductivity and fast ion transport of the electrolyte.

Since PAM possesses good biocompatibility characteristics, it can also be compounded with a biopolymer for enhanced conductivity for ECD applications. This was clearly demonstrated by Pan *et al.* where an ECD gel electrolyte was prepared using cellulose and PMA.^[58] The double network gel was prepared by dropping a precursor solution containing acrylamide monomer, N, N'-methylenebisaryamide and carboxymethylcellulose in between two ITO-glass electrodes and UV light was used to initiate the polymerization process. As anticipated, the composite hydrogel showed higher ionic conductivity than carbocymethylcellulose only and this was linked to the lone pair present in the PAM network. Additionally, the ECD constructed with the composite gel electrolyte displayed enhanced colouration efficiency, better cycling stability and lower power consumption. The reason for this

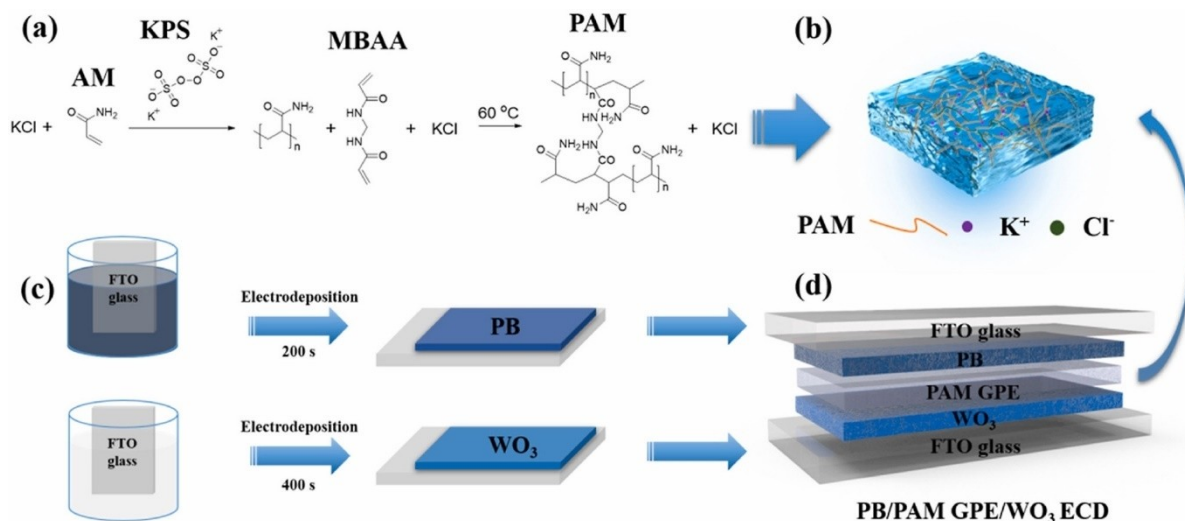


Figure 4. (a) Preparation route of the PAM gel, (b) the structure of PAM gel, (c) the preparation processes of electrochromic films and (d) the assembly of an ECD. (Reproduced with permission from Reference.^[57] Copyright Elsevier 2023).

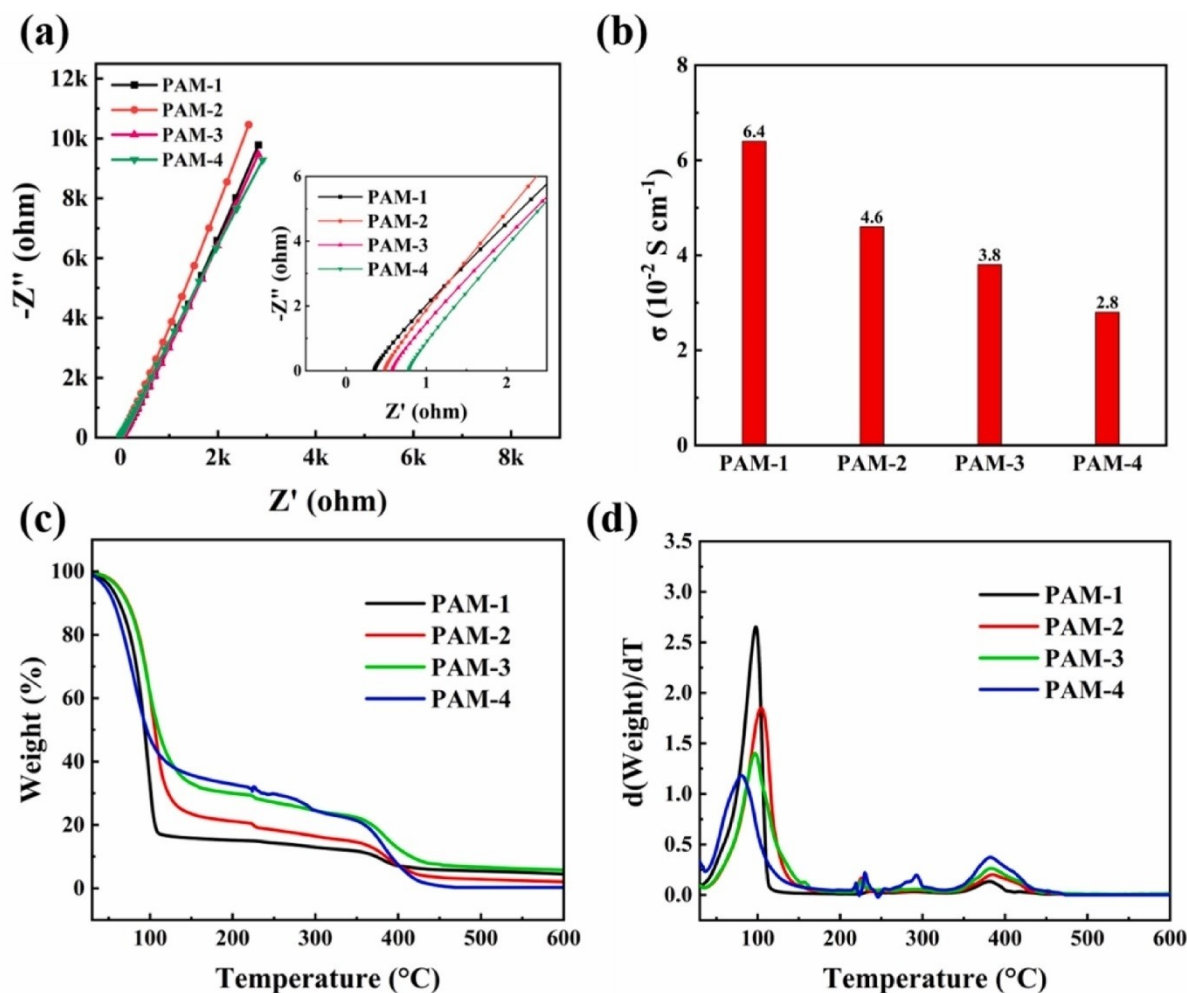


Figure 5. (a) EIS curves (inset: enlarged intercepts with the x-axis), (b) ionic conductivity (1 mol L^{-1} KCl), (c) TG curves and (d) derivative thermogravimetry (DTG) curves of the PAM GPEs with different AM concentrations (Reproduced with permission from Reference.^[57] Copyright Elsevier 2023)

attractive performance was because of the synergistic interactions and hydrogen bonding within the PAM and cellulose networks which favours electrons mobility. Additionally, considering the composite electrolyte is water based, it offers an environmentally friendly applications for wearables, smart windows and electronic displays.

A major constraint to the use of PAM gel electrolytes is the fact that they cannot be used for construction of ECDs that would be exposed to sub-zero temperatures because of water freezing. To overcome this, efforts have been made to expand the temperature operating window of the gels through the incorporation of appropriate ions that could reduce the freezing point of water. A typical example of such an ion is the zinc which is capable of forming strong electrostatic interaction with dipolar water molecules in the gel and thereby limit the freezing point of water. This approach was employed in the study conducted by Ai *et al.* involving the construction of an ECD using zinc modified polyacrylamide electrolyte.^[59] The gel electrolyte was prepared through a facile photopolymerization route whereby zinc chloride, acrylamide monomer, N, N'-methylenebisacrylamide and ammonium persulphate were mixed together to form a precursor solution which was subsequently exposed to UV light. The amount of zinc ion in the gel was optimized by using different concentrations within 1.5 to 9 M of zinc chloride. The conductivity of the electrolyte increased with increasing in zinc concentration until 7.5 M after which the formation of anhydrous ionic groups led to sharp fall in the conductivity. Interestingly, the presence of zinc ion in the gel promoted anti-freezing characteristic in the gel as the gel still showed remarkable conductivities at -10°C and -30°C degrees. Additionally, the ECD fabricated using the gel displayed good colour contrast and impressive cycle stability. The zinc modified PAM gel was also used to construct a large dimension ECD ($100\times 100\text{ mm}^2$) with a good performance but lesser stability than the smaller dimensions ECD. Nevertheless, the findings from this study established that an environmentally friendly and harsh condition resistant ECD can be produced using the PAM.

3.3. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) based electrolytes

Another class of semi-solid electrolytes commonly used for ECD construction are those based on PVDF-HFP. PVDF-HFP is a unique material with enticing chemical and mechanical properties. It has a crystalline portion (PVDF) which makes it highly chemically stable while the HFP, an amorphous portion, makes it a good ionic conducting plasticizer.^[60] Additionally, other materials such as nanoparticles can easily be added to the polymer to further improve its mechanical properties, thermal stability and electrical properties. Hence, its use is attractive for ECDs. An example of research involving the application of PVDF-HFP based electrolyte in all-solid ECDs is the work reported by Xing *et al.*^[61] They prepared a quasi-solid electrolyte of porous PVDF-HFP containing ionic liquid through direct thermal polymerization. The electrochromic material used

consist of oligo(ethylene glycol) imbedded into 3,4-propylenedioxythiophene polymer chain. It was observed that the synergic between the PVDF-HFP electrolyte and the electrochromic material led to significant reduction in the interface resistance, enhanced ion diffusion coefficient and consequently impressive electrochromic activity as noted in the high coloration efficiency and swift switching response. Also, the challenge of poor interface contact between electrochromic materials and quasi-solid electrolytes which often result in poor performance of ECD was greatly overcome in this study. The researchers adopted the approach of preparing the quasi-solid electrolyte through in-situ polymerisation within the ECD. Hence, the electrolyte was found to possess good bond strength (0.8 MPa) and lower interfacial resistance towards the electrochromic material.

However, being a gel electrolyte, the PVDF-HFP electrolyte is still susceptible to gradual degradation, reduced ion mobility and effect of stress and strain. Hence, researchers have identified that the addition of inorganic nanofillers could improve the performance of PVDF-HFP gel electrolyte. A common example of such nanofillers is SiO_2 nanoparticles which has been applied to improve the performance of several polymer gel electrolytes for batteries and supercapacitors.^[62–64] Silori *et al.* demonstrated its use for the improvement of PVDF-HFP electrolyte in the construction of ECD.^[65] The prepared polymer electrolyte was made up of PVDF-HFP, 1-,buty-3-methylimidazolium tetrafluoroborate (BMIMBF_4) and SiO_2 nanofillers. Four types of mesoporous silica which are fine hexagonal pore-type (MCM5), silica (NS), spherical pore-type silica (SPHS) and fumed silica (FMS) were investigated for the impact on the electrolyte properties and ECD performances. The preparation of the electrolyte is summarised in Figure 6. Simply, the precursor solution containing PVDF-HFP, BMIMBF_4 and SiO_2 nanofillers was prepared first and used for electrospinning.

The presence of SiO_2 nanofillers in the electrolyte significantly improved its mechanical properties as evident in the increased tensile strength and elongation as shown in Figure 7. Additionally, the ionic conductivity of the electrolyte was also improved to a value comparable to that of liquid electrolyte. The ECD constructed with the electrolyte showed an astounding stability and coloration efficiency. A similar trend was observed in another study involving a quasi-solid electrolyte made up of PVDF-HFP, PMMA and SiO_2 .^[66] The composite electrolyte showed higher ionic conductivity due to the better dispersion of SiO_2 in the polymer matrix as well as the synergistic effect of PVDF-HFP and PMMA. In addition to this, the gel was found to possess better electrochemical stability and optical properties. Regarding the optical properties, it was observed that without fillers, the gel displayed a good transparency (90% transmittance) and after the addition, the transmittance value decreased with the quantity added and this revealed the need to optimize the amount of fillers used. Nevertheless, the composite gel electrolyte still recorded over 80% transmittance in all cases. From the results reported, it is clear that SiO_2 nanofillers are excellent candidates for modification of PVDF-HFP electrolyte for enhanced electrochromic applications.

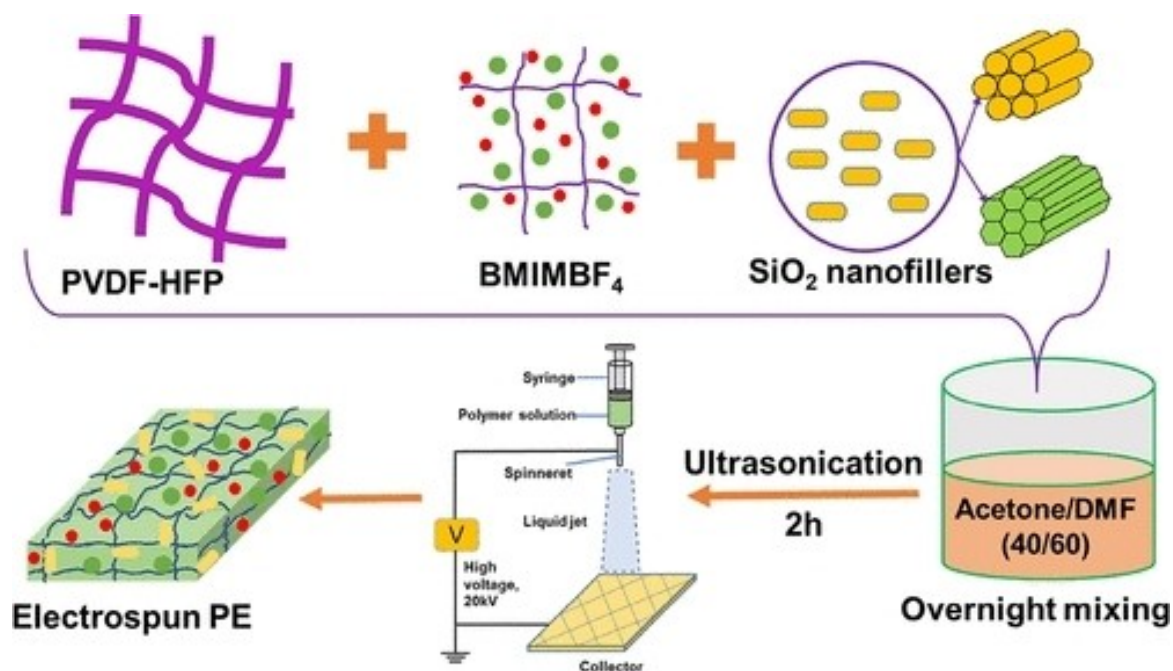


Figure 6. Schematic of the Fabrication Procedure for Filler-Induced Electrospun Polymer Electrolyte (Reproduced with permission from Ref.^[65] Copyright ACS 2023)

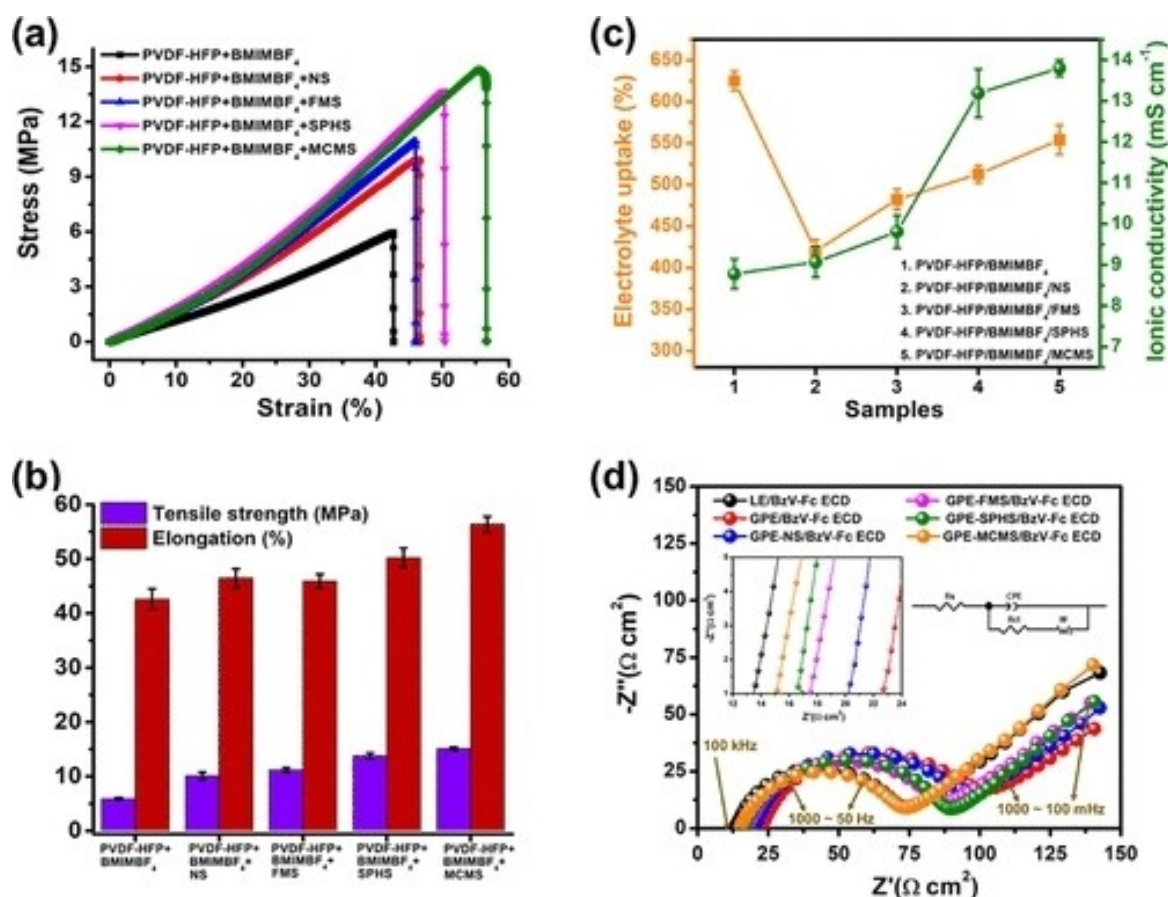


Figure 7. (a) Stress (MPa) vs strain (%) curves for electrospun membranes. (b) Representation of the tensile strength (MPa) and elongation (% strain, ΔL) for the electrospun membranes. (c) EU (%) and ionic conductivity (σ , mS cm^{-1}) of pristine and filler-based PVDF-HFP/BMIMBF₄ membranes at 25 °C. (d) Nyquist plots of representative ECDs. The ECDs were applied to an amplitude of 10 mV (vs OCP) in a frequency range from 10⁵ to 0.1 Hz. (Reproduced with permission from Reference.^[65] Copyright ACS 2023)

Table 2 presents a summary of some recent reports on the use of different kinds of synthesized and commercial gel or quasi solid electrolytes in ECDs. Notably, lithium salts are popular in the composition of the electrolytes. Nevertheless, the use of other salts such as KCl and SiO₂ as fillers have also been observed to produce expected performance of ECD. More importantly, is the fact that the commonly used organic compounds for the gel electrolytes can easily be modified to improve the properties such as ionic conductivities and stability. These gels with or without any fillers or dopants possess good optical properties such as good transparency.

3.4. Stability of ECDs with quasi-solid gel electrolytes

A critical parameter essential for the performance of an ideal ECD is the cyclic stability. It is expected that a good ECD should be able to undergo several cycles of oxidation and reduction without any significant loss to the performance of the electrochromic material and consequently the device. The leakages and entrapment of air peculiar to liquid electrolyte usually impede the cyclic stability of ECD with liquid electrolytes. Since this challenge is overcome in quasi-solid electrolytes, ECDs involving quasi-solid electrolytes could display better cyclic stability. Evidence of this was demonstrated in the work of Halder *et al.*^[43] They observed that the electrochromic material showed an excellent durability according to chronoamperometry cyclic stability over 600 cycles by alternating the voltage between the oxidation and reduction potential with 4 second intervals using either liquid or quasi-solid electrolyte. However, as shown in Figure 8, slight changes in transmittance over the

cycles can be seen in the liquid electrolyte while the PMMA gel electrolyte displayed better stability with no obvious changes in the transmittance values. Similarly, the ECD constructed by Zhou *et al.* with SN modified PMMA as gel electrolyte displayed a good cyclic stability after 500 cycles.^[47] After the 500 cycles the optical modulation of the device only decreased by 2% and the switching property remained stable.

Such outstanding cyclic stability have also been recorded with ECDs consisting of PAM based quasi-solid electrolyte. For example, the ECD prepared by Pan *et al.* with PAM electrolyte retained 99% of the initial percentage transmittance value after 12,000 cycles.^[58] In the absence of PAM the retention value dropped to 95.5% and this equally revealed the ability of quasi-solid electrolyte to facilitate good cyclic stability of ECDs. Similarly, in another study involving PAM gel electrolyte, the ECD recorded an optical modulation of 74.8% after the first cycle which remained unchanged after 500 cycles and still retained 90.6% of the initial optical modulation value after 13,000 cycles.^[57] These studies clearly revealed that the use of quasi-solid electrolyte is for ECD is suitable to improve their cyclic stability which is beneficial to their applications.

4. Conclusion and future perspectives

Electrochromic materials have great potential for applications in wearables, smart windows and energy storage devices and the construction of all solid ECDs on a laboratory scale using quasi solid electrolytes is a major step in achieving the end-user applications. From the above discussions, it is evident that polymers such as polyacrylamide and polymethylmethacrylate

Table 2. Recent studies on the application of quasi-solid electrolytes in ECD.

Matrix	Fillers/salt	Conductivity (mS cm ⁻¹) at 25 °C	CE (cm ² C ⁻¹)	Optics (% Transmittance)	Ref
PAA-HPMC-Ca	Li ₂ SO ₄	54.2	84.6	Transparent (> 95 %)	[67]
NOA65	PC:LiClO ₄	0.06	47.5	Transparent (85 %)	[68]
MASTIFLEX	PC:LiClO ₄	0.65	52	Transparent (> 80 %)	[68]
PMMA	TBATFB	–	544	Transparent	[69]
PNIPAM	LiClO ₄	15.4	342.76	Transparent (≈ 80 %)	[70]
MASTIFLEX	LiClO ₄ + I ⁻ /I ³	–	82.8	Transparent	[71]
PAM-CMC	NaHCO ₃	0.18	168.5	–	[58]
PAM	KCl	64	154.5	Transparent	[57]
SN/PEG	LiClO ₄	–	37	Transparent (> 98 %)	[72]
PMMA	LiClO ₄	–	324	Transparent	[43]
SN/PMMA	LiClO ₄	2.02	–	Transparent	[47]
P(AMPS-co-PEGMA)-PVDF-HFP	LiClO ₄	0.016	–	–	[73]
PEDOT:PSS	LiClO ₄	3×10 ⁻⁷	360	–	[74]
P(MMA-PETA)-PEG/PVDF-HFP	LITFSI	9.5×10 ⁻⁵	918	Transparent	[61]
PVDF-HFP	SiO ₂	13.5×10 ⁻³	276.3	–	[65]
PVDF-HFP/PMMA	SiO ₂	2.22×10 ⁻³	–	Transparent (≈ 80 %)	[66]

PAA-HPMC: Polyacrylic acid-hydroxypropyl methylcellulose. PNIPAM: Poly N-isopropyl acrylamide. P(AMPS-co-PEGMA): poly [(2-acrylamido-2-methylpropane-sulfonic acid)-co-poly (ethylene glycol) dimethacrylate].

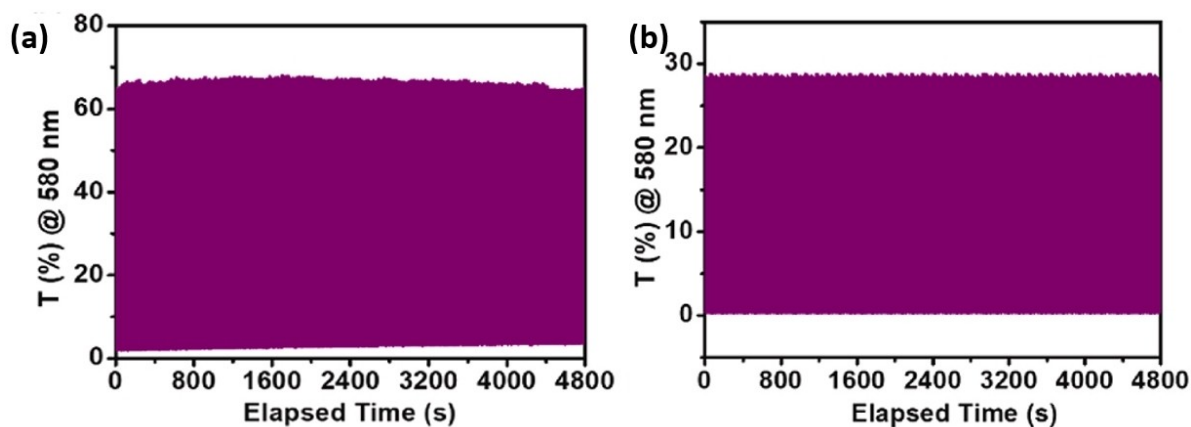


Figure 8. Switching stability of ECD over 600 cycles in a 4 second interval time using (a) liquid electrolyte and (b) quasi-solid electrolyte. (Reproduced with permission from Reference^[43] Copyright Elsevier 2023)

are major compounds that have been employed for the preparation of gel electrolytes for ECDs with organic electrochromic materials. The preparation methods for these electrolytes are simple, reproducible, requires no complex setups and can be easily modified for better optimisation. Additionally, it has been observed that composite gel electrolytes have outperformed their parent compounds and this is because desirable properties can be added to a typical polymer electrolyte by compositing it with a specific compound. Furthermore, some commercial polymers have also been directly used for the construction of all solid ECDs and this further confirms the popularity of quasi-solid electrolytes in ECDs.

However, from the literature discussed, some observations have been noted and hence the following suggested recommendations for future works on the use of gel or quasi-solid electrolytes for ECD construction. Firstly, in the majority of the studies, the dimension of the FTO glass used is relatively small. It will be more advantageous and informative if such devices are upscaled to a reasonable degree within the laboratory as this will help industries interested in making use of this technology on a large scale to make adequate decisions. Another area of concern is the lack of essential electrochromic performance parameters such as coloration efficiency in some reported works. Likewise, in some experimental analysis, the complete description is omitted. These make it difficult to have a fair comparison with other studies where similar materials are employed. In future studies, it is recommended that researchers pay considerable attention to how their findings are reported. Moreover, there still exist a huge gap between the researcher's laboratories and the industries interested in these technologies. More industrial collaborations are therefore encouraged. This will shorten the gap between industries and academic researchers which in turn would shorten the timeframe between the conceptualisation of an idea, its application at the laboratory level and adoption on the industrial scale. Lastly, little is reported on the stability and reusability of the constructed ECDs and the degradation of the gel electrolytes. Future works on this area of research should endeavour to

include these studies. Overall, the use of quasi-solid electrolytes in ECDs is an interesting and fast-growing area of research. With the concerted efforts dedicated to it, the real-life applications of many electrochromic materials in ECDs can be achieved with the use of these gel electrolytes.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Electrochromic devices · gel electrolytes · organic electrochromic materials

- [1] S.-H. Park, J. Lim, I. Y. Song, J.-R. Lee, T. Park, *Adv. Energy Mater.* **2014**, *4*, 1300489.
- [2] G. Liu, L. Zheng, Z. Zhang, Y. Liu, Z. Li, *Electrochim. Acta* **2023**, *440*, 141748.
- [3] H. Gong, A. Li, G. Fu, M. Zhang, Z. Zheng, Q. Zhang, K. Zhou, J. Liu, H. Wang, *J Mater Chem A Mater* **2023**, *11*, 8939–8949.
- [4] J.-L. Wang, S.-Z. Sheng, Z. He, R. Wang, Z. Pan, H.-Y. Zhao, J.-W. Liu, S.-H. Yu, *Nano Lett.* **2021**, *21*, 9976–9982.
- [5] N. Zohrevand, T. Madrakian, A. Ghoorchian, A. Afkhami, *Electrochim. Acta* **2022**, *427*, 140856.
- [6] X. Jiao, G. Li, Z. Yuan, C. Zhang, *ACS Appl Energy Mater* **2021**, *4*, 14155–14168.
- [7] R. J. Mortimer, *Chem. Soc. Rev.* **1997**, *26*, 147–156.
- [8] Y. Zhao, X. Zhang, W. Li, Z. Li, H. Zhang, M. Chen, W. Sun, Y. Xiao, J. Zhao, Y. Li, *Sol. Energy Mater. Sol. Cells* **2022**, *237*, 111564.
- [9] C. Y. Jeong, H. Watanabe, K. Tajima, *Electrochim. Acta* **2021**, *389*, 138764.
- [10] Y. Qian, H. Yang, Y. Wang, *Dyes Pigm.* **2020**, *176*, 108251.
- [11] S. Roy, C. Chakraborty, *Sol. Energy Mater. Sol. Cells* **2020**, *208*, 110392.
- [12] S. Xiao, Y. Zhang, L. Ma, S. Zhao, N. Wu, D. Xiao, *Dyes Pigm.* **2020**, *174*, 108055.
- [13] R. H. Bulloch, J. R. Reynolds, *J Mater Chem C Mater* **2016**, *4*, 603–610.
- [14] C. Preston, Y. Dobashi, N. T. Nguyen, M. S. Sarwar, D. Jun, C. Plesse, X. Sallenave, F. Vidal, P.-H. Aubert, J. D. W. Madden, *ACS Appl. Mater. Interfaces* **2023**, *15*, 28288–28299.

- [15] K. Madasamy, D. Velayutham, V. Suryanarayanan, M. Kathiresan, K.-C. Ho, *J Mater Chem C Mater* **2019**, *7*, 4622–4637.
- [16] H. Wang, M. Barrett, B. Duane, J. Gu, F. Zenhausern, *Mater. Sci. Eng. B* **2018**, *228*, 167–174.
- [17] W. T. Neo, Q. Ye, S.-J. Chua, J. Xu, *J Mater Chem C Mater* **2016**, *4*, 7364–7376.
- [18] J. Jensen, M. Hösel, A. L. Dyer, F. C. Krebs, *Adv. Funct. Mater.* **2015**, *25*, 2073–2090.
- [19] W. K. Thakur, G. Ding, J. Ma, P. S. Lee, X. Lu, *Adv. Mater.* **2012**, *24*, 4071–4096.
- [20] B. Yang, G. Yang, Y.-M. Zhang, S. X.-A. Zhang, *J Mater Chem C Mater* **2021**, *9*, 4730–4741.
- [21] M. H. Azarian, J. Wootthikanokkhan, *Ionics (Kiel)* **2020**, *26*, 5841–5851.
- [22] J. Bae, H. Kim, H. C. Moon, S. H. Kim, *J Mater Chem C Mater* **2016**, *4*, 10887–10892.
- [23] P. Cossari, A. Cannavale, S. Gambino, G. Gigli, *Sol. Energy Mater. Sol. Cells* **2016**, *155*, 411–420.
- [24] A. A. Argun, P.-H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A. G. MacDiarmid, J. R. Reynolds, *Chem. Mater.* **2004**, *16*, 4401–4412.
- [25] T. A. Welsh, E. R. Draper, *RSC Adv.* **2021**, *11*, 5245–5264.
- [26] W. T. Neo, Z. Shi, C. M. Cho, S. Chua, J. Xu, *ChemPlusChem* **2015**, *80*, 1298–1305.
- [27] D. Zhou, B. Che, X. Lu, *J Mater Chem C Mater* **2017**, *5*, 1758–1766.
- [28] M. A. Riza, M. A. Ibrahim, U. C. Ahamefula, M. A. Mat Teridi, N. Ahmad Ludin, S. Sepeai, K. Sopian, *Sol. Energy* **2016**, *137*, 371–378.
- [29] L. C. Lopes, S. Husmann, A. J. G. Zarbin, *Electrochim. Acta* **2020**, *345*, 136199.
- [30] S. Kandpal, T. Ghosh, M. Sharma, D. K. Pathak, M. Tanwar, C. Rani, R. Bhatia, I. Sameera, A. Chaudhary, R. Kumar, *Appl. Phys. Lett.* **2021**, *118*, 153301.
- [31] A. S. Shaplov, D. O. Ponkratov, P.-H. Aubert, E. I. Lozinskaya, C. Plesse, F. Vidal, Y. S. Vygodskii, *Chem. Commun.* **2014**, *50*, 3191–3193.
- [32] T. A. Nguyen, B. S. Soram, D. T. Tran, N. H. Kim, J. H. Lee, *Chem. Eng. J.* **2023**, *452*, 139555.
- [33] T. Li, S. Li, X. Li, Z. Xu, J. Zhao, Y. Shi, Y. Wang, R. Yu, X. Liu, Q. Xu, W. Guo, *Sci Bull (Beijing)* **2020**, *65*, 225–232.
- [34] X. Yang, S. Cong, J. Li, J. Chen, F. Jin, Z. Zhao, *Sol. Energy Mater. Sol. Cells* **2019**, *200*, 109952.
- [35] F. Hu, Y. Xue, N. Jian, K. Qu, K. Lin, X. Zhu, T. Wu, X. Liu, J. Xu, B. Lu, *Electrochim. Acta* **2020**, *357*, 136859.
- [36] H.-C. Lu, S.-Y. Kao, H.-F. Yu, T.-H. Chang, C.-W. Kung, K.-C. Ho, *ACS Appl. Mater. Interfaces* **2016**, *8*, 30351–30361.
- [37] A. S. Shaplov, D. O. Ponkratov, P.-H. Aubert, E. I. Lozinskaya, C. Plesse, F. Vidal, Y. S. Vygodskii, *Chem. Commun.* **2014**, *50*, 3191–3193.
- [38] Y. Ding, M. Wang, Z. Mei, X. Diao, *Sol. Energy Mater. Sol. Cells* **2022**, *248*, 112037.
- [39] C. T. Prontera, N. Gallo, R. Giannuzzi, M. Pugliese, V. Primiceri, F. Mariano, A. Maggiore, G. Gigli, A. Sannino, L. Salvatore, V. Maiorano, *Gels* **2023**, *9*, 310.
- [40] Y. Alesanco, A. Viñuales, J. Rodriguez, R. Tena-Zaera, *Materials* **2018**, *11*, 414.
- [41] G. P. T. Ganesh, R. Ravi, B. Deb, *Sol. Energy Mater. Sol. Cells* **2015**, *140*, 17–24.
- [42] S. Halder, S. Roy, C. Chakraborty, *Sol. Energy Mater. Sol. Cells* **2022**, *234*, 111429.
- [43] S. Halder, C. Chakraborty, *Sol. Energy Mater. Sol. Cells* **2023**, *254*, 112288.
- [44] L. Othman, K. W. Chew, Z. Osman, *Ionics (Kiel)* **2007**, *13*, 337–342.
- [45] L. Xu, Y. Li, Y. Ji, J. Zhang, L. Shao, D. Zhang, L. Ma, G. Gao, Z. Jiang, *Chem. Eng. J.* **2023**, *467*, 143400.
- [46] M. A. Cardoso, S. F. H. Correia, H. M. R. Gonçalves, R. F. P. Pereira, S. Pereira, T. M. R. Maria, M. M. Silva, A. J. M. Valente, E. Fortunato, R. A. S. Ferreira, V. de Zea Bermudez, *J. Sol-Gel Sci. Technol.* **2022**, *101*, 58–70.
- [47] Z. Zhou, Y. Tang, G. Li, G. Xu, Y. Liu, G. Han, *Polymers (Basel)*. **2023**, *15*, 3008.
- [48] M. Zachariah, M. Romanini, P. Tripathi, M. Barrio, J. L. Tamarit, R. Macovez, *J. Phys. Chem. C* **2015**, *119*, 27298–27306.
- [49] J.-Y. Wang, M.-C. Wang, D.-J. Jan, *Sol. Energy Mater. Sol. Cells* **2017**, *160*, 476–483.
- [50] S. Guan, W. Wang, J. Zheng, C. Xu, *Electrochim. Acta* **2020**, *354*, 136702.
- [51] H. J. Lee, C. Lee, J. Song, Y. J. Yun, Y. Jun, C. S. Ah, *J Mater Chem C Mater* **2020**, *8*, 8747–8754.
- [52] S. Cui, Y. Lv, W. Miao, W. Hou, X. Wang, Q. Hu, K. Sun, H. Peng, G. Ma, *J. Energy Storage* **2023**, *73*, 108843.
- [53] Q. Hu, S. Cui, K. Sun, X. Shi, W. Miao, X. Wang, H. Peng, G. Ma, *J. Energy Storage* **2023**, *68*, 107815.
- [54] W. Deng, Z. Zhou, Y. Li, M. Zhang, X. Yuan, J. Hu, Z. Li, C. Li, R. Li, *ACS Nano* **2020**, *14*, 15776–15785.
- [55] H. Miao, B. Chen, S. Li, X. Wu, Q. Wang, C. Zhang, Z. Sun, H. Li, *J. Power Sources* **2020**, *450*, 227653.
- [56] H. Wang, J. Liu, S. Ahmed, T. Wang, S. Song, *J. Energy Storage* **2022**, *56*, 105923.
- [57] H. Cai, Z. Chen, S. Guo, D. Ma, J. Wang, *Sol. Energy Mater. Sol. Cells* **2023**, *256*, 112310.
- [58] M. Pan, Q. He, J. Liu, K. Du, C. Gong, Q. Tang, *Dyes Pigment.* **2023**, *212*, 111126.
- [59] X. Ai, Q. Zhao, Y. Duan, Z. Chen, Z. Zhang, Y. Liu, Y. Gao, *Cell Rep Phys Sci* **2022**, *3*, 101148.
- [60] P. Zheng, J. Qiu, X. Wang, Z. Yu, Y. Ma, T. Li, *J. Appl. Polym. Sci.* **2021**, *138*, 1–9.
- [61] G. Xing, L. Wu, G. Kuang, T. Ma, Z. Chen, Y. Tao, Y. Kang, S. Zhang, *Electrochim. Acta* **2022**, *432*, 141216.
- [62] S. Ketabi, K. Lian, *Electrochim. Acta* **2013**, *103*, 174–178.
- [63] Y. Zhu, J. Cao, H. Chen, Q. Yu, B. Li, *J Mater Chem A Mater* **2019**, *7*, 6832–6839.
- [64] A. Saal, T. Hagemann, U. S. Schubert, *Adv. Energy Mater.* **2021**, *11*, 2001984.
- [65] G. K. Silori, S. Thoka, K.-C. Ho, *ACS Appl. Mater. Interfaces* **2023**, *15*, 25791–25805.
- [66] S. Khan, C. Fang, Y. Ma, M. Ul Haq, M. Nisar, G. Xu, Y. Liu, G. Han, *J. Electrochem. Soc.* **2021**, *168*, 022504.
- [67] W. Li, Y. Cui, *Sol. Energy Mater. Sol. Cells* **2023**, *250*, 112071.
- [68] V. Primiceri, M. Pugliese, C. T. Prontera, A. G. Monteduro, M. Esposito, A. Maggiore, A. Cannavale, R. Giannuzzi, G. Gigli, V. Maiorano, *Sol. Energy Mater. Sol. Cells* **2022**, *240*, 111657.
- [69] M. Icli Ozkut, A. M. Onal, A. Cihaner, *Synth. Met.* **2023**, *296*, 117374.
- [70] B. Deng, Y. Zhu, X. Wang, J. Zhu, M. Liu, M. Liu, Y. He, C. Zhu, C. Zhang, H. Meng, *Adv. Mater.* **2023**, *35*, 2302685.
- [71] R. Giannuzzi, C. T. Prontera, V. Primiceri, A. L. Capodilupo, M. Pugliese, F. Mariano, A. Maggiore, G. Gigli, V. Maiorano, *Sol. Energy Mater. Sol. Cells* **2023**, *257*, 112346.
- [72] C.-L. Lin, A. Chen, *Surf. Coat. Technol.* **2022**, *434*, 128124.
- [73] D. Wang, P. Zheng, Z. Yu, X. Wang, T. Li, *Polym. Int.* **2023**, *72*, 704–710.
- [74] C. Johannes, S. Macher, L. Niklaus, M. Schott, H. Hillmer, M. Hartung, H.-P. Heim, *Polymers (Basel)*. **2023**, *15*, 1982.

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