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# A pragmatic approach to methyl methacrylate based solid polymer electrolyte processing: A case study for electrochromism

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ABSTRACT

Development of inexpensive and flexible solid polymer electrolytes (SPEs) is critically important for the cost-effective electrochromic device (ECD) fabrication. The SPEs are also an integral part of the flexible ECDs which are projected to boost up the ECD's usability in several unexplored areas. Here we report the synthesis of polymethyl methacrylate (PMMA) based aprotic salt ($LiClO_4$) containing SPEs, which are more or less electrochemically benign in the normal ECD operational voltage window. Experiments verified that the developed SPEs have good luminous clarity (transmittance > 92%), high ionic conductivity of the order of $10^{-4}$ S/cm and excellent dimensional stability, all of which are required for the ideal ECD operations. Impedance spectroscopy showed an enhancement in the ionic conductivity and decrease in the solid electrolyte interface (SEI) resistance with increasing salt loading. Two different device configurations using these SPEs were fabricated and then subjected to detailed electrochemical studies. Comprehensive analysis established long term cyclic durability of the SPEs. Prototype ECDs fabricated using these SPEs rendered excellent optical modulation and coloration reversibility.



## 1. Introduction

SPE and gel polymer electrolytes (GPE) are essential components of energy efficient storage or intercalation devices such as batteries, super capacitors, and fuel cells etc. Earlier, researchers attempted to develop ion conducting polymer electrolytes using alkali-metal salt doped poly-ethylene oxide (PEO) based system [1–4]. Unfortunately, the dimensional stability and ionic conductivity of these electrolytes showed a compromise. There were attempts to boost up the mechanical stability without degrading ionic conductivity by fabricating block co-polymers; we came across two useful papers that report such developments [5,6]. A considerable amount of research effort has continued to explore many other potent polymers and polymer composites with varying degrees of success, examples include polyethylenedioxythiophene (PEDOT) [7], polyacrylonitrile (PAN) [8,9], polyethylene glycol, polypropylene glycol [10], polyaniline (PANI) [11], polyvinylidenefluoride (PVDF) [12,13] etc.

The working principle of the ECDs is largely similar to rocking chair type battery operation. The ECDs can reversibly change their optical property when a small voltage (~1 to 3 V) is applied across it. To revert back to the original (bleached/colored) state, a reverse voltage of the same order is required [14,15]. Although, intense research efforts resulted in many developments related to ECD fabrication processes, projected large scale applications of ECDs in buildings and displays have not been realized yet. The main quandary is the cost of an ECD with all its components. For existing buildings, replacing windows with a smart EC window itself presents a huge challenge, both in terms of expenditure and glass waste management. One way of bypassing this problem is to develop flexible lamination type EC devices which could be refitted with an existing window [16]. The cost remained as the main bottleneck for these devices regardless of many attempts by researchers [17]. Baetens et al. [18] reviewed and listed many vendors, who are currently making commercial ECDs. Targeting cost effective solution for ECDs must be associated with reduction of materials and processing costs, and an easily processable and cheap SPE specially optimized for EC applications will immensely help in these respects.

The PMMA is actively studied as host polymer because of its outstanding clarity, film formation capability, salt retention capability coupled with hardness, durability and mechanical stability [19–21]. PMMA has proven weather resistant properties and is therefore attractive for building/outdoor applications. It is required to balance mechanical stability without degrading ionic conductivity and retain dimensional stability of the polymer by balancing amount of alkali metal salt, plasticizer and nano-ceramic

*Abbreviations:* GPE, gel polymer electrolyte; ECD, electrochromic device; SPE, solid polymer electrolyte; SEI, solid electrolyte interface; EPD, electrophoretic deposition; DA-I, device architecture 1; DA II, device architecture 2

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fillers ($Al_2O_3/SiO_2$) [22]. The popular choice of plasticizers was ethylene carbonate (EC) or propylene carbonate (PC) because of their high dielectric constant and their compatibility with PMMA [23,24]. For the specific case of ECD, it must be noted that there are some salient differences in the functional requirements of the ECD electrolytes compared to a battery, such as luminous clarity (as high as possible), durability (years compared to months), cyclic stability (thousands compared to hundreds) and conductivity (less demanding). At some point, one must specially optimize the electrolyte for intended EC applications. Research publications targeting these issues are still minimal [25].

In this work, we adopted an uncomplicated EC device system to understand critical parameters responsible for SPE performance in ECDs. We started with SPE processing using different recipes and then extensively studied their short and long term electrochemical performances. The ECDs were fabricated by sandwiching SPE films between two conducting glass plates, one of which was coated with $WO_{3-x}$ film (detailed fabrication process is discussed in Section 2). The SPE films contain different concentrations of $LiClO_4$ salt and PC (no ceramic fillers). Here we would present experimental evidences leading to following observations which, we believe, will be especially important for low cost ECD development in the future,

1. Polymer processing at right condition is essential for successful ECD operation. Humidity is a major nuisance during processing and the electrolyte constituents should be dehydrated carefully. Glove box processing is preferred but not absolutely required if proper procedure is adopted.
2. As expected, the SPE performances were found to be strongly dependent on the ratio of its components. We noticed a ceiling exists for both salt and plasticizer content in PMMA based SPEs. While excess plasticizer affects dimensional stability, salt concentration degrades luminous transmittance.
3. Higher salt loading facilitates reduction of SEI resistance and increase in ionic conductivity in SPE, which in turn affects ion intercalation inside the active matrix.

The resulting devices show excellent coloration reversibility, good electrochemical stability and high transmittance modulation.

## 2. Experimental

### 2.1. Materials

$WO_{3-x}$ powder was obtained from Alpha aesar (Product no.: 89949). PMMA (CAS# 9011-14-7), PC (CAS# 108-32-7) and $LiClO_4$ (CAS# 7791-03-9) were procured from Sigma-Aldrich. Ethanol and chloroform were procured from the local vendors and doubly distilled before use.

### 2.2. Deposition of $WO_{3-x}$ active matrix

$WO_{3-x}$ films were deposited on a fluorinated tin oxide (FTO) coated glass substrate by electrophoretic deposition (EPD). Ideally in the EPD technique, particles in a colloidal dispersion are made to migrate and then deposit on a conductive surface under a suitable electric field. The details of this process could be found elsewhere [26]. Quasi-stable $WO_{3-x}$ dispersions were prepared by mixing 5 wt% of nano-powder with ethanol using an ultrasonic homogenizer (Sonic® Vibra-cell VCX 500). FTO plates half-immersed in the dispersions were used as the working electrode (substrate) and tungsten wire mesh was used as the counter electrode. We used a precision source meter (Keithley® 2400) for current sourcing. $WO_{3-x}$ films were deposited on cathode for 3 min and after stopping the current flow the FTO plates were lifted out to ensure minimal vibration to maintain excellent homogeneity. XRD analysis showed predominantly oxygen deficient phases of $WO_3$ ($WO_{2.9}$, $WO_{2.92}$, and $WO_{2.8}$) were present in the films.

### 2.3. Electrolyte preparation

Several processing recipes were attempted for electrolyte preparation and then tested using actual device configuration. PC, chloroform and tetrahydrofuran (THF) were mostly used as the solvents. Measured amount of PMMA and $LiClO_4$ salt was dissolved in these solvents and sticky gels/free standing films were formed by controlled ultrasonication. Thermal treatment was necessary in almost all cases to facilitate solvent evaporation. In the subsequent section (Section 3) we have discussed the performance issues of thus prepared electrolytes.

For optimized electrolyte performance in ECDs the constituents must be properly dried to ensure that the water content is absolutely minimal. $LiClO_4$ was dried overnight at 110 °C in a vacuum oven. Measured amount of salt, PC (plasticizer) and PMMA (host, dried at 90 °C, 12 h) were dissolved in THF and stirred for 24 h at room temperature. The mixture is then poured into a clean petri dish and covered by an aluminum foil with small punctures. The solvent was made to evaporate slowly at room temperature under dry nitrogen flow (solvent evaporation could be done inside a hood). Freestanding electrolyte film (~130 to 250 μm thickness) can be peeled off from the petri dish after 24 h. Several electrolyte films with varied salt and plasticizer content were fabricated to study their performance in ECDs.

### 2.4. Materials characterization and electrochemical measurements

Optical characterizations of electrolyte and ECD devices were performed by an UV–visible–NIR spectroscopy using a Shimadzu UV–vis recording spectrophotometer (UV-2600) with $BaSO_4$ as standard. Structural and morphological studies were done using XRD (Analytical X'pert Pro) and SEM (JEOL 5600 LV). A polarized light microscope (PLM, OLYMPUS BX51) was used for optical images of the polymer electrolyte. We measured moisture content of the SPEs by thermogravimetric analysis (Q50 TGA from TA instruments). Cyclic voltammetry (CV, BASI CV-50W) and impedance spectroscopy (Hewlett-Packard 4192A LF) were performed for electrochemical characterization of the films. We used the following two device arrangements for characterization:

1. Device architecture I (DA-I): SPE sandwiched between active electrode ($WO_{3-x}$) and a FTO coated glass plate (Glass/FTO/$WO_{3-x}$/electrolyte/FTO/Glass). Prototype devices were fabricated using the same architecture. Prior using in the device, the surfaces of the SPE were wetted with little amount of THF for the improved adherence.
2. Device architecture II (DA-II): SPE sandwiched between two highly conducting metal (Pt) coated glass plates (Glass/Pt/electrolyte/Pt/Glass).

## 3. Results and discussion

It is well established that standard FTO coating on the glass is responsible for a ~17% reduction of luminous transparency. Therefore highest transparency of ECDs fabricated using FTO coated glass can reach only up to ~66%. To ensure excellent device quality, luminous transparency loss in the electrolyte and the active matrix should be absolutely minimal. The effect of $LiClO_4$ loading on PMMA host is presented in Fig. 1, which showed