



Synthesis of poly(methyl methacrylate)-succinonitrile composite polymer electrolyte and its application for flexible electrochromic devices



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ABSTRACT

This study reports the synthesis of a gel polymer electrolyte (GPE) with enhanced ion transport characteristic, based on the composite polymer of poly(methyl methacrylate) (PMMA) and succinonitrile (SN). Moreover, to demonstrate the practical applications, the GPE was applied to the assembly of the electrochromic devices (ECDs) with both glass and plastic substrates. In this composite polymer electrolyte, PMMA served as the polymer matrix and propylene carbonate (PC) was used as the plasticizer, which also provided better dispersion of the plastic crystal SN within PMMA. The composition ratio of PC to SN was investigated by measuring the ionic conductivity of the GPEs. The optimized ratio of PC to SN was 4:1 with an ionic conductivity of $1.46 \text{ mS} \cdot \text{cm}^{-1}$. For the fabrication of the ECDs, tungsten oxide (WO_3) was used as the cathodic coloring film, which is fabricated by pulsed dc magnetron reactive sputtering. Prussian Blue nanoparticles (PBNPs) were synthesized and coated on the transparent Sn-doped indium oxide (ITO) substrates for the anodic coloring material. The performance of the $5 \times 5 \text{ cm}^2$ WO_3 -PBNPs ECD was confirmed by observing its spectroelectrochemical behaviors. This quasi-solid-state ECD fabricated with the PMMA-SN composite polymer showed an optical contrast of 52.4% at 695 nm. The optical transmittance of the ECD could be reversibly modulated from 57.9% (bleached) to 5.5% (darkened) at 695 nm, by applying potentials of 1.8 and -2.0 V , respectively. During the durability test, the transmittance change (ΔT) of this ECD remained 44.5% after 2250 cycles, which was 85% of its original.

1. Introduction

For the past few decades, the electrochromic materials and devices have attracted lots of interest because of the energy-saving and optical modulation properties [1–6]. Chromism is a phenomenon related to the variation of the optical characteristics of materials accompanied with certain stimuli, which includes electricity (electrochromism), light irradiation (photochromism) and heat (thermochromism) [7–12]. The electrochromic device (ECD) can achieve the optical modulation conveniently by applying the voltage biases. Various chemical compounds have been investigated and developed for the ECDs, such as metal oxides [13,14], inorganic complexes [15,16], organic molecules [17,18], electroactive polymer [19,20] and metallo-supramolecules [21,22]. Moreover, commercialization of some electrochromic systems has been successfully fulfilled, such as smart windows for buildings or airplanes [23,24], electrochromic rearview mirror [25] and sunglasses [26]. Therefore, the promising potential of this technology has been proved, and the development of ECDs has become one of the most popular research topics. Taking practical application into considera-

tion, the electrochromic materials with acceptable transmittance change (ΔT) and long-term stability have been reported [27–30]. For example, tungsten oxide (WO_3) is one of the well-developed materials with durable electrochromic properties, which is a cathodic coloring material [27,28]. Hydrrous nickel oxide (NiO) is also one of the typical electrochromic materials for the anodic coloring material [29,30]. There are a number of studies about the ECDs based on WO_3 and NiO. However, in order to improve the electrochromic performance and replace these transition metal oxides, many novel electrochromic materials, such as small organic compounds viologens [31,32], metallo-supramolecular polyelectrolyte [33,34], conducting polymers [35,36], have been synthesized. Apart from the demand for new materials in the ECDs, the safety and leakage problem of the liquid state devices are the other important issues. This makes solid and gel electrolytes essential alternatives to the liquid electrolytes.

Generally, the function of the electrolyte in the electrochromic system is to provide the ionic connection and prevent the direct electrical contact between the electrodes. There are several kinds of electrolytes, which includes liquid electrolyte, ceramic or inorganic

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solid electrolytes and polymer electrolytes [37–39]. Among the different electrolytes, polymer electrolytes possess several advantages and have gained the attention of researchers, such as low cost, easy processing, good endurance, and high transparency [40]. In addition to the application of ECD, polymer electrolytes are also introduced to other electrical devices, such as lithium-ion batteries [41], fuel cells [42], supercapacitors [43] and organic photovoltaics [44]. Polymer electrolytes can be roughly classified into solid polymer electrolytes (SPEs) and gel polymer electrolytes (GPEs). SPEs are solvent free systems and have ionic conducting characteristics by dissolving the salts into the polymer matrix. For example, poly(ethylene oxide) (PEO), poly(vinyl fluoride) (PVDF), poly(methyl methacrylate) (PMMA) and polyacrylonitrile (PAN) are the commonly used polymer matrices. The ionic conductivity of these systems is low and ranges between 10^{-6} and 10^{-8} S cm^{-1} at room temperature [40]. GPEs are generally composed of the polymer matrix with soluble salt and a suitable liquid plasticizer, which makes this system a stable gel. Owing to the hybrid polymer network structure, GPEs possess both the adhesive and diffusive properties. Besides, a higher ionic conductivity (usually higher than 10^{-4} S cm^{-1}) can be obtained in this two-phase system. With such ion transport characteristics, GPEs probably meet the specifications for commercial products. However, GPEs still lack good mechanical properties compared to SPEs. There are several studies of improving the mechanical properties of GPEs without decreasing its ionic conductivity with different strategies [45–48]. Puguang et al. have reported an ECD with the GPE based on polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) loaded with 3-isocyanatopropyltriethoxysilane (IPTES) functionalized zirconium oxide (ZrO_2) nanoparticles. The ionic conductivity and the transparency of the GPE can be enhanced by incorporating the ZrO_2 nanoparticles [45]. In Cardoso et al.'s work, the GPE consists of poly(oxyethylene) (PEO) and proton ionic liquids [EIm][TfO] is synthesized. This GPE shows good mechanical properties, thermal stability (up to 200 °C) and ionic conductivity (3.2×10^{-4} S cm^{-1}) at 20 °C [46]. Soutar et al. have developed a WO_3 /Prussian Blue (PB) ECD with a UV-curable polymer electrolyte. This GPE is formed by a LiClO_4 -doped hybrid sol gel material containing 3-methacryloxy-propyltrimethoxysilane (MEMO) and zirconium n-propoxide [47]. Lee et al. demonstrates a flexible lithium-ion battery with a porous polyethylene terephthalate (PET) nonwoven as the backbone of the GPE, which is composed of a UV-curable ethoxylated trimethylolpropane triacrylate (ETPTA) monomer and a plastic crystal succinonitrile (SN). The GPE shows unique properties of high ionic conductivity, thermal stability and mechanical strength [48].

Concerning the optical modulation of the ECDs, the transparency is a critical issue for the solid or gel electrolytes. In this study, PMMA with outstanding clarity was chosen as the polymer host for the GPE. In order to improve the performance of the GPE, the plastic crystal SN with good ionic transport capability was introduced into the polymer matrix. The ionic conductivity of the PMMA-SN composite GPE could be enhanced by adding appropriate amounts of plasticizer. The performance of the GPEs with different percentages of the components was also investigated in this work. To confirm the application in ECDs of the PMMA-SN composite GPE, we demonstrated the typical complementary electrochromic system WO_3 /PMMA-SN/PB nanoparticles. The ECD performance presented in this work was studied by the *in-situ* spectroelectrochemistry. The device possessed multiple colors, a good optical contrast of 52.4% and a short response time of < 10 s (90% of the infinite transmittance value). Furthermore, the ECD remained 85% of its original transmittance change (ΔT) after 2250 continuous operations, which gave the comparable cycling stability to previously reported literature studies [49–55].

2. Experimental

2.1. Materials

All chemicals were ACS reagent grade and used without further purification. Poly(methyl methacrylate) (average $M_w \sim 360,000$, Sigma–Aldrich), succinonitrile (99%, Sigma–Aldrich), propylene carbonate (anhydrous, 99.7%, Sigma–Aldrich) and lithium perchlorate (99%, Sigma–Aldrich) were used as to synthesize the PMMA-SN composite GPEs. Optically transparent Sn-doped indium oxide ($\text{In}_2\text{O}_3:\text{Sn}$, or ITO) glass substrates ($R_{\text{sh}} = 6 \Omega/\square$, Uni-onward Corporation, New Taipei City, Taiwan) with dimensions of $5.0 \times 5.0 \times 0.1 \text{ cm}^3$ were used as the conducting substrates for the deposition of electrochromic thin films. Prior to their use, the ITO substrates were cleaned ultrasonically in a 0.1 M HCl solution for 1 min and then in DIW for another 1 min. The substrates were dried in air before use.

2.2. Preparation of the polymer electrolytes

Before preparing the GPEs, the LiClO_4 was dried overnight in a vacuum oven at 100 °C to remove the water. Then LiClO_4 was added into PC to form the PC solution, and the concentration of LiClO_4 in the PC solution was fixed at 0.5 M in this study. A temperature control electric mixer was used for the formation of the PMMA-SN composite GPEs. Measured amount of PC solution and plastic crystal SN were mixed together, and stirred at 80 °C for 1 h. The PMMA powders (25g) were added slowly into the solution, and the mixture was stirred at 150 °C for 8 h with a stirring rate of 500 rpm. The quasi-solid polymer electrolyte was then poured onto a releasing paper ($50 \times 50 \text{ cm}^2$) and cooled in a vacuum oven at 30 °C for 1 h. The PMMA-SN composite GPEs was then covered with another releasing paper and stored in a vacuum sealing bag. To study the ionic conductivity of the GPE, the GPEs prepared with different conditions were sealed between two ITO/glass electrodes by a programmable laminating machine. The sealing condition was described in the [Supplementary material](#), which was the same as the ECD assembly. The electrochemical impedance spectroscopy (EIS) of the PMMA-SN composite GPEs was performed by a potentiostat/galvanostat (Autolab, model PGSTAT 30) under the scanning frequency between 10 Hz and 1 MHz. A micrometer calipers (Digimatic Micrometer MDC-25SX, Mitutoyo, Japan; Resolution=0.001 mm) was used to estimate the thickness of the electrolyte layer of the sealed devices.

2.3. Fabrication of the WO_3 /PMMA-SN/PBNPs ECDs

The preparation processes of the ECDs are described as follows: First, the WO_3 thin-film was prepared on the ITO/glass electrode by pulsed dc magnetron reactive sputtering with the homemade instruments. The thickness of WO_3 was controlled at 170 nm, which were measured by a profilometer (Alpha-Step D-600 Stylus Profiler, KLA-Tencor, USA). A 0.5 cm wide electrical conductive tape (3 M Company) was applied to one side of the ITO as the bus bar. The water-dispersible PBNPs were synthesized according to the previous literature [56] and coated onto the ITO by spray coating at 90 °C. The thickness of PBNPs layer ranged from 190 to 230 nm, and the average thickness value of five different samples was ca. 205 nm. The charge capacities of WO_3 and PBNPs thin film were 20.5 and 17.5 $\text{mC}\cdot\text{cm}^{-2}$ estimated from cyclic voltammetry curves, respectively. The configuration and the photos of the WO_3 /PMMA-SN/PBNPs ECDs were shown as [Fig. 1](#). This sandwich-like device was fabricated by using a programmable laminating machine. To study the spectroelectrochemical performance of the electrochromic thin-film electrodes or the ECDs, a potentiostat/galvanostat (CHI 900B, CHI, USA) and a spectrophotometer (SolidSpec-3700, Shi-madzu, Japan) were utilized. For the demonstration of a flexible ECD with the PMMA-SN composite GPE, a homemade transparent PET/ITO substrate (ITO thickness=150 nm) was substi-

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