



Spectroelectrochemical and adhesion properties of chemically synthesized ion conducting poly (vinyl butyral) in Prussian blue and poly (3, 4-ethylenedioxythiophene) laminated electrochromic glazing

Lee-May Huang^{a,*}, Cheng-Yu Peng^b, Chih-Wei Hu^{c,d}, Hsin-Che Lu^c, Chih-Hung Chen^a,
Dung-Jing Yang^c, Cheng-Chien Kuo^b, Kuo-Chuan Ho^c

^a Green Energy & Environment Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 31040, Taiwan

^b Department of Electrical Engineering, National Taiwan University of Science and Technology, Taipei 10617, Taiwan

^c Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

^d Structural Materials Research Institute, National Institute of Advanced Industrial Science and Technology, Nagoya, Aichi 463-8560, Japan

ARTICLE INFO

Keywords:

Electrochromic device
Prussian blue (PB)
poly (3, 4-ethylenedioxythiophene) (PEDOT)
Chemically synthesized ion conducting-poly
(vinyl butyral) (CSIC-PVB)

ABSTRACT

A novel laminated electrochromic device (ECD) with a chemically synthesized ion conducting-poly (vinyl butyral) (CSIC-PVB) electrolyte is demonstrated. The anodically coloring material and the cathodically coloring material of the device are Prussian blue (PB) and poly (3, 4-ethylenedioxythiophene) (PEDOT) thin films, respectively. From the view of the structure, a laminated electrochromic glazing demands solid polymer electrolyte with both excellent sealing and ionic conductivity properties. The ionic conductivities of the CSIC-PVB films vary in the order of 10^{-3} down to 10^{-6} S/cm, whereas the adhesion strengths of these ion conducting PVB interlayers change from 3 to 11 N/mm². The ionic conductivity and the adhesion of the CSIC-PVB films are proportional to the amount of ionic segments incorporated into the polymer backbone. This PB/CSIC-PVB/PEDOT laminated ECD has an optimal absorbance change at 620 nm. The ECD provides a 39.8% transmittance change (ΔT) at the potential range between 1.0 V and -1.1 V (PEDOT vs. PB), with a bleaching time of 1.2 s and a darkening time of 1.5 s. And the coloration efficiency at 620 nm of the device is calculated to be 270.8 cm²/C.

1. Introduction

Poly (vinyl butyral) (PVB) had already been used as an interlayer in laminated glass in the construction and automobile industries for decades. Recently, the applications of PVB have been extended to enhance the standard of safety of laminated solar cell module glass in building-integrated photovoltaic (BIPV) [1]. This polymeric material has a benefit of tough but highly elastic, with strong bonding and excellent mechanical properties. PVB can be classified as a copolymer consisting of non-polar butyral group and highly polar vinyl alcohol group. The high adhesion of PVB is achieved through reversible weak hydrogen bond between the alcohol groups of the PVB and silanol groups on the glass surface [2,3].

Besides its excellent adherence to glass, PVB has been investigated for possible applications as solid polymer electrolyte layer in electrochromic (EC) device [4–7]. The low glass transition temperature, and the presence of amorphous domain within the PVB polymer complex are two essential factors for increasing the ions transfer in the electrolyte.

Switchable electrochromic device (ECD) has been developed for retrofitting existing windows, to dynamically control solar heat gain, daylight, glare and view. The optical absorption of the device changes in response to an externally applied electric field or current [8]. A complementary EC device is typically five layers, and is deposited on a glass substrate. The electrochromic stack consists of an anodically coloring layer, an electrolyte layer, and a cathodically coloring layer, sandwiched between two transparent conducting oxide layers. The glazing switches between clear and tinted state, as the electric field distributed ions move reversibly through the electrolyte layer.

EC materials are generally categorized into three types: the inorganic materials, the organic small molecule materials, and the polymer materials. The inorganic materials have good stability and thermal resistance, such as Prussian blue (PB), tungsten oxide (WO₃), and nickel oxide (NiO_x) [9,10]. The purely synthetic PB (ferric hexacyanoferrate(II)) pigment was discovered in the early 18th century. PB has two categories according to its potassium salts peptization: the soluble one (KFe^{III}[Fe^{II}(CN)₆]) and the insoluble one (Fe^{III}[Fe^{II}(CN)₆]₃). The organic materials have become attractive for its potential in

* Corresponding author.

E-mail address: lmhuang@itri.org.tw (L.-M. Huang).

tunable color application through molecular design, and one of the most well-known organic small molecule for this field is the viologen [11]. Polypyrrole, polyaniline, polythiophene and their derivatives [12,13] are some examples of conducting polymers use as EC materials. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the poly(3,4-alkylenedioxythiophene) (PXDOT) families which appears deep blue in neutral state and becomes colorless upon doping.

From the view of the structure, a laminated electrochromic glazing demands solid polymer electrolyte with both excellent sealing and ionic conductivity properties. The idea of integrating the adhesion and the ion conducting functions of PVB into a single electrolyte layer was previously reported by Kraft et al. [14,15]. The well-known technology for the production of conventional PVB interlayer can be used for the manufacture of the ion conducting PVB, while the electrochromic glazing can be produced with standard laminated safety glass equipment.

To our knowledge, early reports of ion conducting PVB mainly focus on blending alkaline metal salts with the PVB; additional plasticizers are sometimes added for increasing the ionic conductivity of the polymer electrolyte [6,14]. The effects of different alkaline salts and solvents are shown to have a direct bearing on the conductivity values. However, none of these studies discusses the effect of chemically synthesized ion conducting electrolyte layer on the performance of electrochromic glazing

PVB is a polyacetal produced by the condensation of polyvinyl alcohol with n-butyraldehyde in the presence of an acid catalyst. The condensation reaction produces 1,3-dioxane rings but it is not taken to completion, leaving some unreacted hydroxyl groups which promote good adhesion to the glass substrate on lamination [16]. The chemically synthesized ion conducting-PVB (CSIC-PVB) was developed by using an ion-containing aldehyde in addition to butyraldehyde during the acetalization of poly(vinyl alcohol) [17,18]. The BSNA-PVOH reaction is temperature limited, the acetal formation is severely hindered above 60 °C, due to the occurrence of hydrolysis reaction that causes the disproportionation of vinylbenzal sulfonate groups. The final CSIC-PVB obtained at the end of the reaction comprises of poly(vinyl butyral), poly(vinyl benzal sodium sulfonate) and residual poly(vinyl acetate) and poly(vinyl alcohol) groups [17].

The purpose of incorporating ionic functional group is to bring about thermally reversible thermoplastic behavior of PVB, attributed to the morphological structures formed due to ionic associations, as reported in the early study [18]. This thermally reversible property allows easy processability of the PVB at elevated temperatures and high modulus at ambient temperatures, making the PVB very versatile. However, despite thorough study in the rheological and thermal characteristics, the ion conducting and the adhesion performances of the ion conducting PVB was not reported by the authors.

In this work, the ionic conductivity and adhesion behaviors of CSIC-PVB are explored. The CSIC-PVB is constituted of a charged copolymer containing both electrically neutral repeating units and a fraction of ionic group covalently bonded to the polymer backbone. The effectiveness of the dual properties of the CSIC-PVB is verified by analyzing the spectroelectrochemical performance of the PB/CSIC-PVB/PEDOT laminated ECD, and by evaluating the adhesion strength of the glass/CSIC-PVB/glass and PB/CSIC-PVB/PEDOT laminated ECD structures.

2. Experimental

2.1. Materials

FeCl₃ (97%), K₃Fe(CN)₆ (> 99%), KCl (99%), HCl (37%), 3,4-ethylenedioxythiophene (EDOT) (97%), LiClO₄ (> 98%), PVOH (molecular weight 89,000–98,000, > 99% hydrolyzed) (> 99%), PVOH (molecular weight 124,000–186,000, > 99% hydrolyzed) (> 99%), sodium salt of o-benzaldehyde sulfonic acid (BSNA) (> 95%), HNO₃ (65%), BA (99%) were all purchased from Sigma Aldrich.

Cetyltrimethylammonium bromide (CTAB) (99%) was purchased from Merck, n-butanol (> 99.9%) from Echo, KOH (> 85.0%) from Showa, tetra-n-butylammonium perchlorate (TBAClO₄) (> 99%) and propylene carbonate (PC) (99%) from Alfa Aesar, PVOH (degree of polymerization (DP) of 2,000, degree of hydrolysis (DH) of 78–82%) were purchased from TCI, and acetonitrile (ACN) (100%) from J.T. Bayker.

2.2. Preparation of electrochromic thin film

0.5 mM K₃Fe(CN)₆, 0.5 mM FeCl₃, 0.1 M KCl, 0.92 mM CTAB, and 0.02 M HCl solution composed the precursor solution for PB preparation [19]. The PB thin film was electrodeposited on Indium Tin Oxide (ITO) glass with an active area of 2 cm × 2 cm by cyclic voltammetric electrodeposition (with platinum foil as a counter electrode), and a potential sweep from – 0.1 to 0.6 V (vs. Ag/AgCl) at a scan rate of 100 mV/s. Whereas PEDOT thin film was electrodeposited from 0.1 M TBAClO₄, and 10 mM EDOT monomer in ACN solution at a constant potential of 1.2 V (vs. Ag/Ag⁺).

2.3. Synthesis of ion conducting PVB

The CSIC-PVB was chemically synthesized by partially acetalizing PVOH with BA in an aqueous medium under acidic conditions [17]. The physical characteristics of PVOH depend on the degree of polymerization and the degree of hydrolysis. In this study, fully hydrolyzed PVOH (with MW = 89,000–98,000 and MW = 124,000–186,000) and partially hydrolyzed PVOH (with DP = 2000) were used to synthesize the CSIC-PVB. The synthesis scheme is depicted in Fig. 1. Different amounts of ion-containing aldehyde (BSNA) were added into 1.2 g PVOH in 30 mL 0.1 M HNO₃ solution and stirred for 2 h at room temperature. BSNA with 0.5, 1, 1.5, 2, 2.5, 3 g, were denoted as sample A, B, C, D, E, F, accordingly. Then, an adequate amount of BA was introduced into the system and stirred for another 4 h. Afterwards, the samples were washed with 0.1 M KOH and dried to obtain fine white powder ion conducting PVB. The samples were all heated to 80 °C to dissolve in n-butanol. Once all the solvent had evaporated, the samples were left behind as sticky and soft PVB films. The CSIC-PVB had very clear transparency, even after been exposed in air as free standing films for more than one week. The UV/Vis/NIR spectrum measurement of the CSIC-PVB film is shown in Fig. 2.

2.4. ECD assembly

Before the assembly of the ECD, the PB and PEDOT thin films were subjected to cyclic voltammetry in 0.1 M LiClO₄/PC in 3 cycles at a scan rate of 100 mV/s from 0.4 to – 0.9 V (vs. Ag/Ag⁺), and from 0.3 to – 1.2 V, respectively. Then, the synthesized ion conducting PVB film with a thickness of 0.5 mm was laminated in-between the PB and PEDOT electrodeposited ITO glasses in their colorless states.

2.5. Measurements

Spectroelectrochemical data of the PB and PEDOT thin films were obtained in-situ, using a potentiostat/galvanostat (model PGSTAT 30, Autolab) and a UV–vis UV-Vis spectrophotometer (model UV-1601 PC, Shimadzu, Japan). 10H¹H NMR spectrum was recorded on a Bruker AMX400 spectrometer, and FTIR spectrometer (Perkin Elmer Spectrum One) were used to identify the functional groups and to confirm the ionic bond formation of CSIC-PVB.

3. Results and discussion

3.1. Ionic conductivity of CSIC-PVB

The reason for better conductivity with the addition BSNA is due to the ionic dissociation of sodium sulfonate ionic segment in poly(vinyl

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