



A novel ionic liquid with stable radical as the electrolyte for hybrid type electrochromic devices



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ABSTRACT

An ionic liquid (IL), 1-butyl-3-{2-oxo-2-[(2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl)amino]ethyl}-1H-imidazol-3-ium tetrafluoroborate (TILBF₄), containing a stable radical, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), was synthesized successfully. The TILBF₄ shows two distinctive properties having the characteristics of ion-storage and supporting electrolyte materials. In this study, a hybrid electrochromic device (ECD) with a high coloration efficiency based on this TILBF₄ and a poly(3,3-diethyl-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine) (PProDOT-Et₂) thin film was proposed. The maximum absorbance of the PProDOT-Et₂/TILBF₄ ECD was noticed at 590 nm upon applying the cell potential between -1.0 and 1.0 V. The device exhibits a transmittance change (ΔT) of 62.2% at 590 nm when being switched in the first transition, with short switching times of 4.0 s for bleaching and 3.6 s for coloring. A relatively high coloration efficiency (η) of 983.0 cm²/C was achieved at 590 nm. Furthermore, the ECD maintained 98.0% of its initial ΔT after consecutive operation for 1000 cycles between -1.0 and 1.0 V.

1. Introduction

Electrochromism is a phenomenon of certain electro-optical materials undergoing redox reactions with reversible color changes [1–3]. This phenomenon is under increasing attention both from the aspects of scientific challenge and industrial application. To date, technological applications of electrochromic device (ECD) have been found in rear-view mirrors smart windows, sunglasses, monitors, displays, and so on [4–8]. Generally, the ECD can be divided into three kinds of structures: (1) solution type, (2) thin-film type, and (3) hybrid type ECD. In the hybrid type ECD, one of the electrochromic materials is coated on the conducting substrate in the form of a thin film, while the other redox species is dissolved in the electrolyte.

The coloration efficiency (η) is considered as one of the judgmental indexes for evaluating electrochromic materials and devices, which is defined as the optical density change divided by the passed charge density at a specific wavelength. A list of literatures, covering both inorganic and organic thin film working electrodes, on the performance of hybrid type ECDs is given in Table 1 [9–25]. To our surprise, only few studies reported the value of η for the hybrid type ECDs. The motivation in this study is to fabricate a stable hybrid ECD with a high η value. Here we propose a hybrid ECD based on a conducting polymer thin film and a novel ionic liquid, so as to achieve a high η value with

long-term stability.

In order to maintain electrochemical balance in an ECD, it was proposed to add another redox species to get the charge balance in the device [26–29]. In general, the ion-storage material could be a redox species in the form of an electroactive material. A stable molecule, namely, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), is a suitable candidate as redox species [25]. The nitro-oxygen radical (N-O•) of TEMPO is protected by its steric structure; therefore the TEMPO shows a good chemical stability in an organic solvent [30]. Moreover, the N-O• of TEMPO has a high intrinsic heterogeneous rate constant, approximately 10⁻¹ cm s⁻¹, which demonstrates that it has the advantage of offering fast electron-transfer in an electrochemical reaction [31]. Takahashi et al. used TEMPO-carrying polymer as the redox active sites in the electrolyte of an ECD; their proposed ECD needed only a low driving voltage and exhibited a long open-circuit memory [32]. Lee et al. synthesized a TEMPO-carrying material, and used it as an electroactive material for lithium batteries [33]. The above-mentioned devices showed high stability, owing to the presence of TEMPO-carrying polymer or species in their electrochemical devices.

Ionic liquids (ILs), composed of organic cations and various anions, have recently received much attention in electrochemical science, owing to their distinctive physicochemical properties. Comparing to conventional liquids such as water, polycarbonate, and acetonitrile, ILs

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Table 1

A list of literatures on the performance of hybrid type ECDs.

Working	Electrolyte	Counter	V_c/V_b^y (V)	λ_{\max} (nm)	η (cm ² /C)	ΔT^z (%)	Ref.
WO ₃	LiI +NH ₄ I+LiClO ₄ in γ -BL ^l	ITO	-1.0-1.0	–	–	60	[9]
Ag/WO ₃	Fc ⁺ phenothiazine+LiClO ₄ + in tetramethylene sulfone+PC	ITO	-1.4-0.0	–	–	16	[10]
PANI	ethyl viologen diperchlorate in PC	ITO	1.0-0.0	550	–	48	[11]
WO ₃	ICS-PPG ^k +BD ^l +KI+I ₂ in AcOH ^m	Pt/ITO	-2.0-2.0	634	–	73 [*]	[12]
WO ₃	ICS-PPG+BD+KI+I ₂ in AcOH	Pt/FTO	-2.0-2.0	634	–	45	[13]
WO ₃	POSS-ionic liquid ⁿ	Pt/FTO	-1.0-1.7	–	–	–	[14]
PB ^o	HV ^o +KCl in IPP ^o / H ₂ O	ITO	1.0-0.0	609	–	59	[15]
WO ₃	EO ₂ -TMSPI ⁺ Im ⁻ +I ₂ in LiOH	Pt/FTO	-1.5-1.7	634	–	50	[16]
V ₂ O ₅	BTFSL ^j in PC	ITO	-0.5-1.5	450	–	25	[17]
BPBD ^b /TiO ₂	LiClO ₄ +Fc in γ -BL	FTO	-1.0-1.0	608	170	55	[18]
BPPBD ^c /TiO ₂	LiClO ₄ +Fc in γ -BL	FTO	-1.0-1.0	656	219	–	[18]
PANI/PA-S ^d	LiClO ₄ +PEO ^e in PC	ITO/PET	-3.5-1.8	600	–	34	[19]
DDP-A ^e	PEO+HV+Bu ₄ NBF ₄ in PC	ITO	1.0-0.0	–	–	–	[20]
DDB-P ^f	PEO+HV+Bu ₄ NBF ₄ in PC	ITO	1.0-0.0	–	–	–	[21]
PEDOT: PSS	PVP ^g +EC ^h +TBAP ^v in EtOH	ITO	-3.0-3.0	–	–	–	[22]
Fe-MEPE ^g	PMMA ^w + LiClO ₄ in PC	ITO	-2.5-2.5	–	–	–	[23]
PEDOT ^h	TEMPO+HV+TBABF ₄ ^x in PC	ITO	1.5~-0.5	610	91	68	[24]
PProDOT-Et ₂	TEMPO+LiClO ₄ in PC	ITO	-0.9-0.5	590	–	59	[25]
PProDOT-Et ₂	TILBF ₄ +LiClO ₄ in PC	ITO	-1.0-1.0	590	983	62	This work

^a Prussian blue^b Bis-(2-phosphonoethyl)-4,4'-bipyridinium dichloride^c 1,1'-Bis-(2-phosphonomethyl 4-phenyl)-4,4'-bipyridinium dichloride^d Polyacrylate-silica^e N,N'-dimethyl-N,N'-diphenyl-1,4-phenylenediamine-acetaldehyde^f N,N'-dimethyl-N,N'-diphenylbenzidine-propionaldehyde^g Metallo-supramolecular polyelectrolytes with iron(II)^h Poly(3,4-ethylenedioxythiophene)ⁱ γ -butyrolactone^j Ferrocene^k 3-isocyanatopropyltriethoxy silane-poly(propyleneglycol)-bis-(2-amino-propyl)ether^l Butanediol^m Acetic acidⁿ 1-methyl-3-propyl hepta(*i*-butyl) octasilsesquioxane imidazolium iodide^o Heptyl viologen^p Isopropanol^q 1-(2-(2-methoxyethoxy)ethoxy)ethyl)-3-(3-(trimethoxysilyl)propyl)imidazolium iodide^r Bis(trifluoromethane)sulfonimide lithium^s Poly(ethylene oxide)^t Polyvinylpyrrolidone^u Ethylene carbonate^v Tetrabutylammonium perchlorate^w Poly(methyl methacrylate)^x Tetrabutylammonium tetrafluoroborate^y V_b and V_c represent the bleaching and coloring potential biases, respectively.^z All transmittance changes (ΔT) listed here include the absorbance of two conducting substrates, except for the case marked with "**".

have attracted considerable interest due to their advantages, such as high thermal stability [34], high chemical stability [35,36], high ionic conductivity [37,38], environment-friendly [39], wide electrochemical windows [40], and negligible vapor pressure [41]. Those properties render ILs ideal candidates in electrolyte research. Using ILs as a supporting electrolyte could increase the conductivity and further improve the performance of ECDs [42]; they also have been proposed as the electrolytes in other electrochemical systems, including dye-sensitized solar cells [43–45], supercapacitors [46–48], and Li-ion batteries [49–51].

In this study, a versatility ionic liquid, 1-butyl-3-(2-oxo-2-((2,2,6,6-tetramethylpiperidin-1-oxyl-4-yl)amino)ethyl)-1H-imidazol-3-ium tetrafluoroborate (TILBF₄), was synthesized through the combination of 1-butylimidazole tetrafluoroborate (BIBF₄) and TEMPO. The material was utilized not only as the electrolyte in the proposed ECD, but also acted as its ion-storage material. Compared to TEMPO, TILBF₄ showed high thermal stability. The proposed ECD, containing a thin film of poly(3,3-diethyl-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine) (PProDOT-Et₂) as the cathodically coloring material and TILBF₄ as both the ionic liquid and ion-storage material, exhibited a transmittance change (ΔT) of 62.2% at 590 nm upon the application of ± 1.0 V. Furthermore, the ECD showed excellent cycling stability over 1000 cycles.

2. Experimental

2.1. Chemicals

Propylene carbonate (PC, $\geq 99.0\%$), acetonitrile (ACN, 99.8%), 4-amino-2,2,6,6-tetramethylpiperidine (98%), and chloroacetyl chloride (C₂H₂Cl₂O, $\geq 99.0\%$) were obtained from Fluka. 1-Butylimidazole (98%), dichloromethane (DCM, $\geq 99.5\%$), hydrogen peroxide (H₂O₂, 30 wt% in H₂O), lithium perchlorate (LiClO₄, 99.99%), potassium tetrafluoroborate (KBF₄, $\geq 99.99\%$), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 98%), 3,3-diethyl-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine (ProDOT-Et₂, 97%), hydrochloric acid (HCl, 37%), and tungstic acid (H₂WO₄, $\geq 99.0\%$) were obtained from Sigma-Aldrich.

2.2. Substrates

Indium-tin oxide (ITO, Solaronix SA, R_{sh}=7 Ω/\square) glasses, as the conducting substrates, were cleaned using neutral cleaner, deionized water, acetone, and isopropanol sequentially. The epoxy tape (3 M Company, 60 μm thick) was used to fix the active area to be 1.0 \times 1.0 cm². A conducting copper tape (3 M Company, 2.0 \times 0.5 cm²) was used as the bus bar at one side of the ITO glass.

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