



Investigations of ionic liquids on the infrared electroreflective properties of poly(3,4-ethylenedioxythiophene)



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ABSTRACT

A semi-interpenetrating network including branched poly(ethylene oxide), nitrile butadiene rubber, and poly(3,4-ethylenedioxythiophene) used for infrared electroemissive device applications has been investigated using a screening of various ionic liquids based on imidazolium, piperidinium and pyridinium cations and fluorosulfonimide, trifluoromethane sulfonimide and tetrafluoroborate anions. Prior to device characterization and in order to have a better understanding of the influence of these ionic liquids on PEDOT-based devices, PEDOT films have been first synthesized by galvanostatic method. Cyclic voltammetry in 3-electrodes configuration of PEDOT layers in the whole set of ionic liquids have demonstrated a significant role of the cation in the redox process. In the case of the devices, the ionic mechanism has been identified by a simple and fast method consisting in studying the volume change of the PEDOT active layer. Among the 8 ionic liquids studied, 7 of them have shown the cation as the predominant mobile specie while, for one of them, both anions and cations were predominantly mobile species depending on time constant. Electrochemical, ionic conductivity and IR-optical properties of the devices swollen with the different ionic liquids have been then investigated. The devices behave in a similar manner both electrochemically and optically. Reflectivity contrasts can reach 27% over a wavelength range of 2.5–20 μm , demonstrating the potential efficiency of such devices for thermal regulation of satellites in a space environment.

1. Introduction

Since many years, electrochromic materials have been extensively studied [1,2]. The modulation of their optical properties after application of an electrical low voltage makes them suitable candidates for various applications in the visible spectral region such as smart windows, anti-glare car rearview mirrors or optical displays [3–8]. These materials can also be used in the infrared spectral region notably in reflective mode for camouflage or thermal control of satellites [7,9–11], this latter being discussed in this article.

In the field of heat control of satellites, depending on the position of the satellite (facing the sun or in the shadow of the earth), an adaptive control of heat fluxes is necessary [12,13]. Thermal regulation is mainly achieved using mechanical louvers and loop heat pipes [14,15]. Nevertheless, these technologies possess drawbacks such as high cost, significant board weight, and high power consumption. Various types of technologies are under study as an alternative to such systems and

among them, electroemissive devices (EED) [8,12,13,16–18]. The EED systems present the advantages of being lighter and less expensive. Their use allows the emissivity modulation of radiating surfaces under the application of a potential in the similar manner as electrochromic materials operating in the visible.

The EED active layer can be made of a metal oxide such as tungsten oxide [8] or of an electronically conducting polymer (ECP) [11,19–21]. In the latter case, the modulation of the optical properties of the active layer is achieved by changing the doping state of the polymer. Applying an electrical low voltage on the active layer, the conducting polymer can switch from a high IR transparent state (neutral) to a high IR-absorption when oxidized. Thus interesting change in the IR-optical properties of the device can be expected if the IR-active ECP layer is prepared on gold surface [22–24]. The active surface is similar to a dual material, *i.e.* ECP + gold. Indeed, in the neutral state, the active surface has a low emissivity since ECP and gold surface are IR-transparent and IR-reflective respectively. In the oxidized state, the active layer displays

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a high emissivity since no IR-reflexion on the gold layer is expected due to the strong IR absorption of the oxidized ECP layer.

Among the electronically conducting polymers, polyaniline (PANI) is one of the most widely used for the fabrication of EED. In 1999, Topart et al. have studied a multilayer EED with polyaniline protonated with camphor sulfonic acid (PANI-CSA) as active layer [7]. Their system has demonstrated good performances at 12 μm with emittance ranging from 0.35 to 0.8 by applying voltages lower than 1.0 V. EEDs based on PANI copolymers have also been developed. For example, Chandrasekhar et al. have reported an emittance variation of 0.3–0.4 in the 2.5–45 μm range using polyaniline/poly(diphenyl amine) (PANI-PDPA) [10]. Other ECP have also been used as active layer of EED. Among them, Reynold's group has investigated the IR emittance of the poly(3,4-propylenedioxythiophene) (PProDOT-Me₂) as active layer. They have obtained an emissivity variation beyond 0.5 over a spectral range of 3–5 μm [19].

On another hand, our laboratory has developed a one-block-based EED composed of a semi-interpenetrating network architecture (semi-IPN) including poly(ethylene oxide) (PEO), nitrile butadiene rubber (NBR), and poly(3,4-ethylenedioxythiophene) (PEDOT) [25–27]. As no gold layer is present, the PEDOT is not only the electroactive layer but also the whole active surface. Hence the EED works in full reflexion/absorption mode. This type of architecture offers the advantage of being single bloc from the active surface through the counter-electrode. The PEDOT is interpenetrated on both sides of the PEO/NBR host matrix, playing both the role of counter-electrode and active layer and preventing delamination issues. However, the thickness of the interpenetrated PEDOT layer ($\sim 2 \mu\text{m}$) is such that whatever the doping state, the ECP layer is never IR-transparent. Nevertheless, as reported by Heeger et al. [23], the PEDOT layer has a high reflectance in the oxidized state because of its electronic conductivity. Thus the emissivity (reflectivity) in the oxidized state is lower (higher) than that in the neutral state. As a consequence, no gold surface as substrate for the ECP is necessary anymore. This approach considerably simplifies the EED fabrication compared to literature's devices mentioned above.

In order to achieve fast electro-commutation, the EED must be swollen by an adequate electrolyte. In most cases, the electrolyte is an organic solvent or gel containing salt. However ionic liquids (IL) have appeared as an interesting alternative to conventional electrolytes [28,29]. They offer a large electrochemical window (4–6 V) providing a better stability of conducting polymers. Moreover, as non-volatile liquids, they could be very well adapted to space applications. Nevertheless, only few studies have been undertaken regarding incorporation of ionic liquids into electroemissive devices [16,30–32]. A screening of different ionic liquids could thus be interesting for assessing their behaviour within the EED.

In this paper, PEO/NBR/PEDOT semi-IPNs used for EED applications have been investigated using a screening of various ionic liquids (ILs) as electrolytes. These ILs were chosen according to the nature and the size of the anion or cation. Electrochemical, electronic conductivity and IR-optical properties of the assembled devices swollen with the different ILs have been studied. In order to better understand the influence of these ILs on PEDOT layer, electropolymerized PEDOT films have been synthesized and electrochemically characterized in the different ILs. On another hand, the ionic conductivity of each PEO/NBR and IL combination has been checked in order to make efficient electroactive devices. Through the combined study of model PEDOT layers and PEO/NBR/PEDOT semi-IPNs, different behaviors have been highlighted depending on the electrolyte including the ion mechanism involved in the redox process.

2. Experimental part

2.1. Materials

Nitrile butadiene rubber with 44% acrylonitrile content (NBR,

$M_w = 230 \text{ kg/mol}$, Perbunan 4456 F Lanxess), poly(ethyleneglycol) dimethacrylate (PEGDM, $M_w = 750 \text{ g/mol}$, Aldrich), poly(ethylene glycol) methyl ether methacrylate (PEGM, $M_w = 450 \text{ g/mol}$, Aldrich), dicumyl peroxide (DCP, $M_w = 270 \text{ g/mol}$, Aldrich), anhydrous Iron chloride (FeCl_3 , $M_w = 162 \text{ g/mol}$, Acros), dicyclohexylperoxydicarbonate (DHPC, $M_w = 296 \text{ g/mol}$, Groupe Arnaud) were used as received. 3,4-ethylenedioxythiophene (EDOT, $M_w = 142 \text{ g/mol}$, Bayer) was purified by distillation under vacuum before use. ILs used were 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI, $M_w = 391 \text{ g/mol}$, Solvionic, 99%), 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (AMITFSI, $M_w = 403 \text{ g/mol}$, Solvionic, 99.5%), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMITFSI, $M_w = 419 \text{ g/mol}$, Solvionic, 99.5%), 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide (MPPPTFSI, $M_w = 422 \text{ g/mol}$, Iolitec, 99%), 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMIFSI, $M_w = 291 \text{ g/mol}$, Solvionic, 99.5%), 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide (Pyr₁₄FSI, $M_w = 322 \text{ g/mol}$, Solvionic, 99.5%), 1-butylpyridinium tetrafluoroborate (BuPyBF₄, $M_w = 223 \text{ g/mol}$, Iolitec, 99%), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄, $M_w = 198 \text{ g/mol}$, Solvionic, 98%). The chemical structures of the ILs used are shown in Fig. 1.

2.2. Preparation of conducting polymer based semi-IPN

The PEO/NBR host matrix was synthesized by an in situ method as described in literature [33]. The obtained IPN films were swollen with 5% of EDOT and immersed for 2 h into a FeCl_3 organic solution (0.25 mol/L) at 50 °C. After the EDOT polymerization, the obtained film was washed several times with methanol to remove the excess of FeCl_3 and the edges were removed out to avoid short circuits between the two PEDOT electrodes. The PEO/NBR/PEDOT semi-IPNs were then dried at room temperature under vacuum for 24 h. Fig. 2 represents the architecture of the final PEO/NBR/PEDOT semi-IPN.

2.3. Electropolymerization of EDOT

The electropolymerizations were performed at constant current, using a potentiostat/galvanostat (VSP 150, Biologic Scientific Instrument), in a one-compartment cell with a Platinum electrode ($S = 0.02 \text{ cm}^2$) as working electrode. A stainless steel was used as counter-

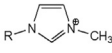

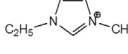
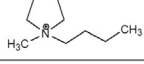

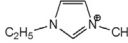
Ionic Liquid	Cation	Anion
EMITFSI	$\text{R} = \text{C}_2\text{H}_5$	
BMITFSI		$\text{R} = \text{C}_4\text{H}_9$
AMITFSI	$\text{R} = \text{C}_3\text{H}_6$	$(\text{CF}_3\text{SO}_2)_2\text{N}^-$
MPPPTFSI		
EMIFSI		$(\text{FSO}_2)_2\text{N}^-$
Pyr ₁₄ FSI		
BuPyBF ₄		BF_4^-
EMIBF ₄		

Fig. 1. Chemical structures of the ionic liquids used.

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