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Electrochromic devices incorporating biohybrid electrolytes doped with a lithium salt, an ionic liquid or a mixture of both

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ABSTRACT

The sol-gel method was employed in the synthesis of di-urethane cross-linked poly(ε-caprolactone) (PCL (530))/siloxane biohybrid ormolytes incorporating either a mixture of lithium triflate ($LiCF_3SO_3$) and the ionic liquid (IL) 1-ethyl-3-methyl imidazolium tetrafluoroborate ($[Emim]BF_4$), or solely with $[Emim]BF_4$ or $LiCF_3SO_3$. The ormolyte doped with $[Emim]BF_4$ is thermally more stable and exhibits higher ionic conductivity (4×10^{-4} and 2×10^{-3} S cm^{-1} at 36 and 98 °C, respectively) than those containing the $LiCF_3SO_3$/$[Emim]BF_4$ mixture or just $LiCF_3SO_3$. The three ormolytes were employed in the production of glass/ITO/ormolyte/WO_3/ITO/glass electrochromic devices (ECDs) designated as ECD@Y with Y = Li-$[Emim]BF_4$, $[Emim]BF_4$ and Li. The three ECDs displayed fast switching speed (ca. 30 s). ECD@Li-$[Emim]BF_4$ exhibited an electrochromic contrast of 18.4% and an optical density change of 0.11 in the visible region, the coloration efficiency attained at 555 nm was 152 and 80.2 cm^{2}C^{-1} in the "on" and "off" states, respectively, and the open circuit memory was 48 hours. In the "on" state the CIE 1931 color space coordinates were x = 0.29 and y = 0.30, corresponding to blue color.

1. Introduction

The use of electrochromic (EC) [1] materials in "smart windows" [2] for the construction of new eco-friendly buildings with environmental and economic benefits [3] makes this class of materials extremely attractive, thus justifying the intense research carried out in the last decades. Anti-glare mirrors [4], helmet visors [5], goggles [6] and sensors [7] are also interesting applications of ECs, some of them having already reached commercialization. The development of electrochromic devices (ECDs) is an active field of research that has resulted in the publication of a significant number of patents [8–10]. A typical ECD comprises five components: a glass substrate (GS), a transparent conducting oxide (TCO) (usually indium tin oxide (ITO)), an EC coating (normally tungsten oxide (WO_3) [11]), an ion conductor (IC) (often a polymer electrolyte (PE)) and an ion storage (IS) coating.

The electrolyte for an ECD must be designed to fulfill the following requirements: (1) Sufficient ionic conductivity; (2) High transparency and (3) Electrochemical stability over the potential window needed to induce the color transition. The sol-gel method [12] is one of the preferred routes to synthesize electrolytes with such features. Typically, the as-produced materials are polymer/siloxane hybrid networks [13], known as ormolytes (organically modified silicate electrolytes) [14], doped with ionic salts, usually composed of monovalent cations. With the primary goal of developing safe electrolytes with increased ionic conductivity [15] to enhance the long term stability and cyclability of the ECD and decrease in parallel its switching time, an ionic liquid (IL) may be included in the electrolyte formulation.

ILs are organic molten salts containing a bulky organic cation that is weakly coordinated to an organic or inorganic anion [16–18]. The unique properties offered by these compounds (e.g., low melting point, chemical and thermal stability with low flammability, negligible vapor pressure, high ionic conductivity

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and broad electrochemical window) have attracted the attention of the energy materials community [19,20], opening new frontiers in the fields of energy storage (e.g., batteries and supercapacitors [21,22]) and energy conversion (e.g., Grätzel-type dye-sensitized solar cells [23,24] and fuel cells [25]). In the last few years it has been recognized that ILs also offer a land of opportunities for ECDs [26–32].

Lu et al. [26] reported early in 2002 unprecedented results for several displays, including electrochromic windows, made from three types of π-conjugated polymers (polyaniline, polypyrrole, and polythiophene) and environmentally stable, room-temperature ILs composed of 1-butyl-3-methylimidazolium cations [$Bmim^+$] together with anions, such as the tetrafluoroborate or hexafluorophosphate ions (BF_4^- and PF_6^-, respectively). Several ECD systems containing gel electrolytes incorporating ILs as plasticizers were later described in the literature [26,29–31,33–37].

In the last few years our group has devoted considerable effort to the development of green prototype ECDs incorporating sol-gel derived di-urethane cross-linked siloxane-based biohybrid electrolytes including poly(ε-caprolactone) (PCL(530), where 530 is the average molecular weight of the polymer in $g\,mol^{-1}$) segments. PCL is a linear, aliphatic thermoplastic, biocompatible, permeable, hydrophobic and biodegradable poly(ester), non-toxic for living organisms. The d-PCL(530)/siloxane matrix was doped with potassium triflate (KCF_3SO_3) [38] and mixtures of lithium triflate ($LiCF_3SO_3$) and europium triflate ($Eu(CF_3SO_3)_3$) [39], and $LiCF_3SO_3$ and erbium triflate ($Er(CF_3SO_3)_3$) [40]. The main goal of the present work has been to produce and characterize an ECD doped with a mixture of $LiCF_3SO_3$ and the 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4) IL (Scheme 1). For comparative purposes ECDs incorporating ormolytes doped solely with either [Emim]BF_4 or $LiCF_3SO_3$ have also been studied.

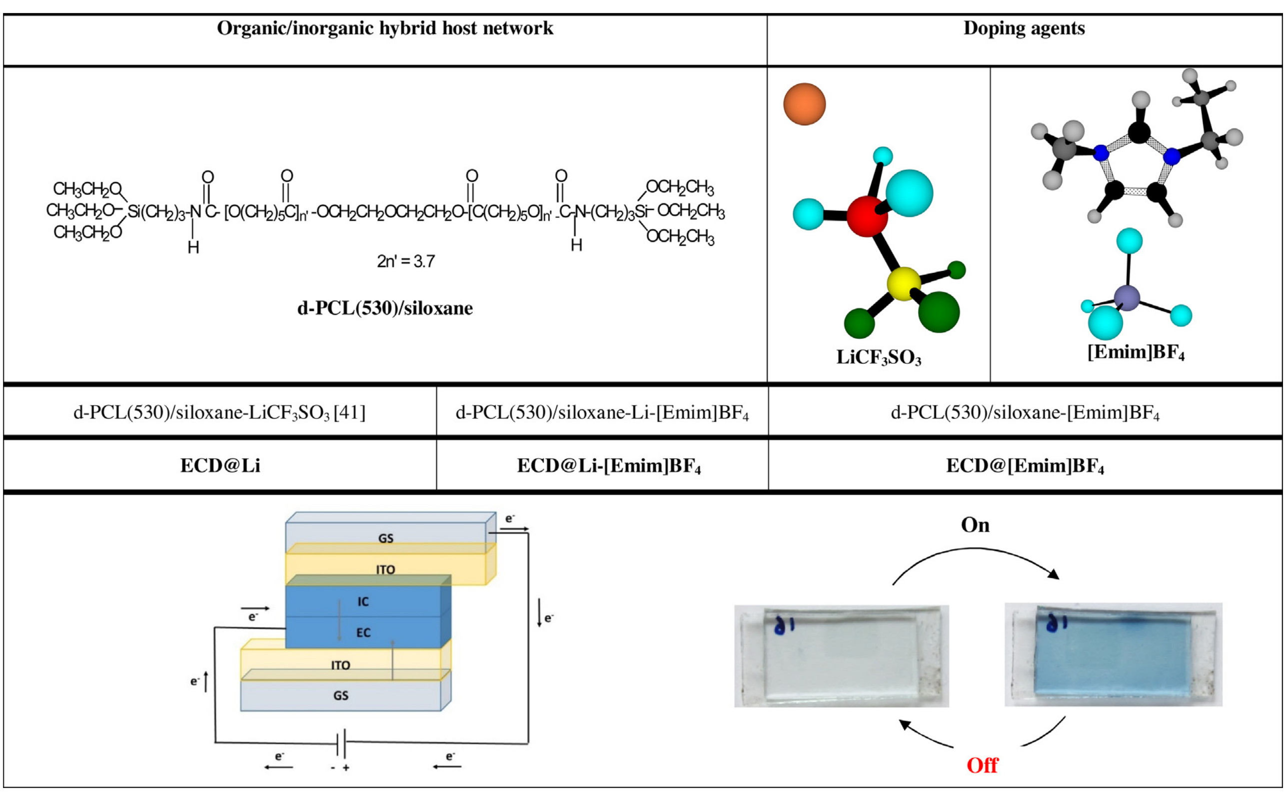
2. Experimental

2.1. Materials

α,ω– hydroxyl poly(ε-caprolactone) (PCL(530), Fluka, average molecular weight 530 $g\,mol^{-1}$) and 3-isocyanatepropyltriethoxysilane (ICPTES, Fluka), $LiCF_3SO_3$ (99.995%, Aldrich) and [Emim]BF_4 (98%, Solvionics) were used as received. Ethanol (CH_3CH_2OH, Merck) and tetrahydrofuran (THF, Merck) were stored over molecular sieves. High purity distilled water was used in all experiments.

2.2. Synthesis of the ormolytes

The synthesis of the ormolytes was performed in two steps according to the method described elsewhere [41]. In the first step a cross-link between the isocianate (—N=C=O) group of ICPTES and the terminal hydroxyl (—OH) group of PCL(530) (Scheme 1, top left) was formed. In the second step appropriate amounts of ethanol, water and salt and/or IL (Scheme 1, top right) were added in order to obtain the desired concentration. Two drops of each sol were employed in the construction of the ECDs. The remaining volumes were transferred to Teflon molds and aged at an oven at 40 °C for 15 days. Experimental details of the synthetic procedure are found in Table S1 of Supplementary Information. The resulting xerogels were identified using the notation d-PCL(530)/siloxane-**Y**, where d means di, PCL(530)/siloxane corresponds to the biohybrid network and **Y** is the doping agent, i.e., Li (only $LiCF_3SO_3$), [Emim]BF_4 (only IL) or Li-[Emim]BF_4 (a mixture of $LiCF_3SO_3$ and [Emim]BF_4). Table S1 of Supplementary Information also provides information on n (composition), which corresponds to the number of ($C(=O)(CH_2)_5O$) repeat units of PCL(530) per Li^+, IL or the



Scheme 1. Overall view of this work: organic/inorganic hybrid matrix and doping agents used (top) to synthesize the electrolytes employed (middle) for the construction of the ECDs (bottom). The pictures show a representative ECD in the as-deposited and colored states. (For interpretation of the references to color in this text, the reader is referred to the web version of this article.)