



Eco-friendly sol-gel derived sodium-based ormolytes for electrochromic devices



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ABSTRACT

The sol-gel method was employed in the preparation of organic/inorganic biohybrid ormolytes composed of a di-urethane cross-linked poly(ϵ -caprolactone) (PCL(530))/siloxane matrix doped for the first time with different amounts of sodium triflate ($\text{NaCF}_3\text{SO}_3 \cdot x\text{H}_2\text{O}$). The samples are semi-crystalline and thermally stable up to ca. 250 °C. The maximum ionic conductivity (4.1×10^{-7} , 1.5×10^{-4} and $8.8 \times 10^{-4} \text{ S cm}^{-1}$ at 30, 49 and 97 °C, respectively) was attained at $n' = 6$, where n' (composition) corresponds to the number of ester ($\text{C}(\text{=O})(\text{CH}_2)_5\text{O}$) repeat units of PCL(530) per sodium ion. Selected ormolytes were employed in the construction and characterization of prototype electrochromic devices (ECDs). Tests with ECDs incorporating poly(oxyethylene)/siloxane ($\text{U}(600)_n\text{NaCF}_3\text{SO}_3$ (where n is the ratio of ether (OCH_2CH_2) repeat units per sodium ion) ormolytes already reported were also performed. The devices exhibited fast switching time of ca. 30 s. At 555 nm the **ECD@U600₆₃Na** device exhibited the highest optical density value ($\Delta(\text{OD}) = 0.12$) and coloration efficiency for bleaching ($\text{CE}_{\text{out}} 131 \text{ cm}^2 \text{ C}^{-1}$, 50th cycle) and good optical memory. The **ECD@PCL₅₈Na** device exhibited a CE value for coloration (0.12 versus 0.061) similar to that of **ECD@U600₆₃Na** ($\text{CE}_{\text{in}} - 116 \text{ cm}^2 \text{ C}^{-1}$, 50th cycle) and a very good stability. However the $\Delta(\text{OD})$ value for the latter device was much higher.

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1. Introduction

Electrochromic (EC) materials [1] and electrochromic devices (ECDs) [2–8] have attracted much interest in the last decades due to the potential technological applications. Among the most popular commercial applications are rear-view mirrors for cars [9], information displays [10], “smart windows” for architecture purposes [11] and aircrafts [12], and goggles and sunglasses [13,14].

A considerable part of the research in the field of ECDs is focused on the development of suitable polymer electrolytes (PEs) [15]. PEs, which are composed of a host macromolecule and a guest salt, have been widely investigated in the field of solid state electrochemistry aiming applications in ECDs [16,17], advanced batteries and fuel cells [18,19]. PEs are advantageous with respect to liquid electrolytes due to their low cost, easy fabrication into thin films, low weight and no leakage. Poly(oxyethylene) (POE) [20,21] is an exceptional host macromolecule which dissolves a wide variety of lithium and sodium salts [22–26].

The tremendous effort devoted to the development of lithium-based electrolyte systems in the last two decades is justified by the successful commercialization of Li-ion batteries in the 1990s. However, nowadays sodium is considered a valuable alternative to lithium because of its low cost, natural abundance and non-toxicity. The recent upsurge of interest in the sodium technology is the answer to the demanding lithium market and the recognition

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that lithium sources are limited. Not only is sodium more abundant, and therefore cheaper, but the batteries made from it may hold more power, charge more quickly and have a longer lifespan. This explains why sodium batteries are rapidly becoming a reality [27–32]. The first prototype of sodium battery, known as a Na-ion cell, was developed by RS2E-Research network on electrochemical energy storage, a French research center on batteries and supercapacitors [33]. Research on PEs composed of sodium salts and different host polymers has been intense in the last few years [34–39]. For instance, attractive PEs based on poly (acrylonitrile) (PAN) doped with sodium triflate (NaCF_3SO_3), with and without ethylene carbonate as plasticizer, exhibited higher ionic conductivity values than the corresponding lithium-based analogues [38].

In the present study we have prepared a set of new eco-friendly ormolytes (organically modified silicate electrolytes) doped for the first time with a wide range of NaCF_3SO_3 concentration and based on a biohybrid host matrix incorporating short poly(ϵ -caprolactone) (PCL(530), where 530 is the average molecular weight in g mol^{-1}) segments covalently bonded through an urethane ($-\text{NHC}(=\text{O})-$) group to siliceous domains. PCL is a synthetic biopolymer extensively employed as suture in the biomedical field [40]. The hybrid electrolytes have been synthesized by the sol-gel process [41], a suitable method to prepare organic/inorganic host hybrid frameworks [42] able to accommodate extremely high contents of guest ionic salts, while avoiding salting-out effects. Our group has devoted considerable efforts to the development of PCL(530)/siloxane hybrid electrolytes doped with various mono-, di- and trivalent salts [43–49]. The performance of some of these systems was tested in prototype ECDs [46–49]. According to the nomenclature adopted previously [43–49] we have designated this family of compounds by means of the notation d-PCL(530)/siloxane_nNaCF₃SO₃.xH₂O, where d means di and n' (composition) corresponds to the number of ester ($\text{C}(=\text{O})(\text{CH}_2)_5\text{O}$) repeat units of PCL(530) per sodium ion. The samples, obtained as thin, transparent films have been examined by means of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD), scanning electron microscopy (SEM), polarized optical microscopy (POM) and complex impedance spectroscopy. To evaluate the cation/urethane and cation/anion interactions Fourier Transform Infrared (FT-IR) and Raman (FT-Raman) spectroscopy were employed.

The ultimate goal of this work has been to test prototype ECDs including d-PCL(530)/siloxane_nNaCF₃SO₃ ormolytes. For comparative purposes two prototype devices incorporating ormolytes doped with NaCF_3SO_3 and based on a di-urea cross-linked POE/siloxane (di-ureasil) host matrix, characterized in a previous work [39], and displaying ionic conductivity values of the same order of magnitude of those exhibited by optimized d-PCL(530)/siloxane_nNaCF₃SO₃ samples, have been also prepared. These materials were represented by the notation d-U(600)_nNaCF₃SO₃ (where U means urea ($-\text{NHC}(=\text{O})\text{NH}-$) group, 600 represents the average molecular weight (in g mol^{-1}) of the starting organic precursor, corresponding to 8.5 ether (OCH_2CH_2) repeat units, and n (composition) is the ratio of OCC repeat units per sodium ion di-ureasil ormolytes. The performance of the ECDs has been evaluated by means of visible (VIS) spectroscopy, cyclic voltammetry (CV) and chronoamperometry (CA).

2. Experimental part

2.1. Materials

α,ω -Hydroxyl poly(ϵ -caprolactone) (PCL(530), Fluka, average molecular weight 530 g mol^{-1}), 3-isocyanatepropyltriethoxysilane (ICPTES, 95%, Fluka) and $\text{NaCF}_3\text{SO}_3 \cdot x\text{H}_2\text{O}$ (99.99%, Aldrich) were used as received. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Merck) and tetrahydrofuran

(THF, Merck) were stored over molecular sieves. High purity distilled water was used in all experiments.

2.2. Synthesis of the d-PCL(530)/siloxane_nNaCF₃SO₃ ormolytes

The synthesis was performed in two steps according to the method described elsewhere [46] which is a modification of that reported for the LiCF_3SO_3 -doped analogues [43]. The progress of the reaction was monitored by FT-IR. The strong vibration due to the isocyanate group of ICPTES at 2271 cm^{-1} became progressively weaker, as the intensity of the bands due to the presence of the urethane groups formed increased concomitantly. In the second stage of the synthetic procedure, a mass of $\text{NaCF}_3\text{SO}_3 \cdot x\text{H}_2\text{O}$ (Table S1 of Supporting Information) was dissolved in this solution. After the evaluation of the amount of water present in the salt by TGA and the deduction of the hydrated salt formula ($\text{NaCF}_3\text{SO}_3 \cdot 1.4\text{H}_2\text{O}$), the composition of the samples (n' and n) were recalculated (Table S1 of Supporting Information). A mixture of ethanol and water (molar ratio 1 ICPTES:4 EtOH:1.5 H₂O) was then added to promote the hydrolysis and condensation reactions. The solution was stirred at room temperature for 30 min, cast onto a Teflon mould, covered with Parafilm and left in a fume cupboard for 24 h. After this time the mould was transferred to an oven at 40°C and the sample was aged for one month. The most relevant experimental details of the synthetic procedure are collected in Table S1 of Supporting Information. Xerogels with compositions ranging from n'=6 to 114 were obtained as transparent monoliths.

2.3. Synthesis of the d-U(600)_nNaCF₃SO₃ ormolytes

The preparation of the d-U(600)_nNaCF₃SO₃ ormolytes was performed according to the procedure reported elsewhere (Table S2 of Supporting Information) [39].

2.4. Experimental techniques

2.4.1. TGA and DSC

The thermogravimetric analyses were performed in a Q500 TA Instruments equipment in the $31\text{--}800^\circ\text{C}$ temperature range at $10^\circ\text{C min}^{-1}$, using a mass of 10–20 mg. Nitrogen was employed as purging gas (40 mL min^{-1} (balance gas) and 60 mL min^{-1} (sample gas)). The thermal behaviour of the xerogels was also determined using a Setaram DSC 131 Differential Scanning Calorimeter. A disk section with a mass of approximately 10–20 mg was removed from each ormolyte film, placed in a $40 \mu\text{L}$ aluminium can and hermetically sealed. To record the thermograms each sample was heated from 25 to 150°C at $10^\circ\text{C min}^{-1}$. High purity nitrogen at a constant flow rate of 35 mL min^{-1} was used as purging gas.

2.4.2. XRD

XRD measurements were performed at room temperature with a PANalytical X'Pert Pro equipped with a X'Celerator detector using monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) over the 2θ range between 10 and 60° . The samples were not submitted to any thermal pre-treatment.

2.4.3. SEM

The HR-SEM/EDS images were obtained at CEMUP-Porto using a FEI QUANTA 400 FEG/EDAX Pegasus X4M financed by the FCT "National Scientific Re-equipment Program" and integrated in the RNME – National Electron Microscopy Network. Prior to being analyzed the samples were coated with Au/Pd.

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