Sol-gel-derived potassium-based di-ureasils for "smart windows"

S. C. Nunes,^a V. de Zea Bermudez,^{*a} M. M. Silva,^b M. J. Smith,^b D. Ostrovskii,^c R. A. Sá Ferreira,^d L. D. Carlos,^d J. Rocha,^e A. Gonçalves^f and E. Fortunato^f

^aDepartamento de Química and CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5000-911 Vila Real, Portugal. E-mail: vbermude@utad.pt; Fax: +351 259 350 480; Tel: +351 259 350 253

^bDepartamento de Química, Universidade do Minho, Gualtar, 4710-057 Braga, Portugal. E-mail: mjsmith@quimica.uninho.pt; Fax: +351 253 678 983; Tel: +351 253 676 376

^cDepartment of Applied Physics, Chalmers University of Technology, 41296 Göteborg, Sweden. E-mail: dostr@fys.chalmers.se; Fax: +46 317 723 177; Tel: +46 317 728 038

^dDepartamento de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal. E-mail: lcarlos@fis.ua.pt; Fax: +351 234 370 298; Tel: +351 234 370 946

^eDepartamento de Química and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal. E-mail: rocha@dq.ua.pt; Fax: +351 234 370 730; Tel: +351 234 370 084

^fDepartamento de Ciência dos Materiais/CENIMAT, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal. E-mail: emf@fc.unl.pt; Fax: +351 212 948 562; Tel: +351 212 948 562

Sol-gel-derived KCF₃SO₃-doped di-urea cross-linked poly(oxyethylene) (POE)/siloxane (di-ureasil) ormolytes with $\infty > n \geq 1$ (n is the number of oxyethylene units per K⁺ ion) have been analysed. Samples with $n > 40$ are thermally stable up to 310 °C. At $n \geq 100$, POE crystallites are present. At $n = 5$, a crystalline POE-KCF₃SO₃ complex with stoichiometry 1 : 1 is formed. In the xerogel with $n = 1$ this complex coexists with free salt. The highest ionic conductivity is reached at $n = 20$. The redox stability domain of this material spans 5.0 V. "Free" anions and weakly coordinated CF₃SO₃⁻ ions appear to be the main charge carriers at $n = 20$. The K⁺ ions interact with the urea carbonyl oxygen atoms at all salt concentrations. Complexation of the cations by POE occurs at $n \leq 20$. In the latter composition range, contact ion pairs and higher ionic aggregates develop. The ormolytes were successfully used in the assembly of prototype electrochromic devices (ECDs) that exhibit good electrochemical stability and demonstrate a memory effect. The ECD incorporating the ormolyte with $n = 20$ displays an average transmittance in the visible region of ca. 90% in the coloured state and of 85–95 % in the bleached state. The corresponding change in colour, evaluated on the basis of the Commission Internationale d'Éclairage (CIE) colour-coordinates system, is reversible: from yellow (0.38, 0.37) for the bleached state to blue (0.29, 0.29) for the coloured state.

Introduction

Electrochromic materials have attracted increasing interest in the last three decades.¹ The colour of these compounds may be electrochemically switched in a reversible and persistent manner (in general from a transparent or "bleached" state to a coloured or "written" state). Electrochromic materials may find use in controllable light-reflective or light-transmissive devices for storage and display of optical information, anti-glare automobile rear- and side-view mirrors, sunglasses, protective eyewear for military use, aircraft canopies with controllable optical transmission, glare-reduction systems for buildings or "smart windows", and reactive labels.^{2–6}

A conventional solid-state electrochromic device (ECD) has a two-electrode sandwich-like configuration in which the electrochromic electrode is separated from a counter-electrode by a solid (e.g., polymer) electrolyte. Colour changes occur by charging–discharging this electrochemical cell through the application of an electrical potential. An interesting feature of some ECDs is that once they are coloured, the applied voltage can be switched off and the colour retained (memory effect). The electrochromic electrode, which may operate in a reflective or transmissive mode (displays and "smart windows", respectively), is composed of a thin layer of electrochromic material deposited onto a transparent electronically conducting oxide film (e.g., tin-doped indium oxide (ITO))⁷ or gallium-doped zinc oxide (ZnO-Ga)⁸-coated glass (or plastic) sheet⁹. Typically the electrochromic material is a transition metal oxide that can exhibit several valence states upon reduction.

For most applications, electrochromic materials are required to exhibit high contrast ratio, high colouration efficiency (absorbance change/charge injected per unit area), high cycle life and high write-erase efficiency (% of originally formed colouration that may be subsequently electro-bleached). While displays demand fast response times, in "smart windows" response times up to several minutes are acceptable.³ Tungsten trioxide (WO₃), by far the most widely studied electrochromic material, undergoes reversible optical switching from white/yellow to dark blue, as a result of an electrochemical process based on simultaneous injection and extraction of electrons and ions (double injection).¹⁰

In recent years the sol-gel method¹¹ has become a popular way for producing ECDs.¹² This versatile synthetic route is advantageously applied to the preparation of high quality electrochromic coatings. Some organic-inorganic sol-gel-derived hybrid materials¹³ have also been proposed as electrolytes in ECDs.¹⁴ With respect to classical polymer electrolytes, ormolytes (acronym of organically modified silicate electrolytes) offer a series of benefits, in particular an essentially amorphous character, high transparency, better mechanical resistance, improved chemical/thermal stability and the ability to solubilise greater quantities of guest salts, avoiding phase separation or "salting-out".

The high ionic conductivity exhibited by polymer electrolyte systems (conventional or hybrid) incorporating K⁺ ions^{15–19} prompted us to investigate in the present work the morphology, structure, thermal properties, ionic conductivity and ionic

electrolytes in ECDs.¹⁴ With respect to classical polymer electrolytes, ormolytes (acronym of organically modified silicate electrolytes) offer a series of benefits, in particular an essentially amorphous character, high transparency, better mechanical resistance, improved chemical/thermal stability and the ability to solubilise greater quantities of guest salts, avoiding phase separation or "salting-out".

The high ionic conductivity exhibited by polymer electrolyte systems (conventional or hybrid) incorporating K⁺ ions^{15–19} prompted us to investigate in the present work the morphology, structure, thermal properties, ionic conductivity and ionic association of a family of potassium triflate (KCF₃SO₃)-doped poly(oxyethylene) (POE)/siloxane xerogels with potential application as ormolytes in the fabrication of "smart windows". The host hybrid framework employed, designated as d-U(2000), belongs to the class of *di-ureasils*,^{20–22} a series of hybrid networks in which the organic and inorganic components are bonded through urea groups. The sample with the highest ionic conductivity has been applied in the fabrication of a glass/ZnO–Ga/d-U(2000)_nKCF₃SO₃/WO₃/ZnO–Ga/glass ECD.

Experimental

Materials

Potassium trifluoromethanesulfonate (KCF₃SO₃, Aldrich) and α,β -diaminepoly(oxyethylene-co-oxypropylene) (commercially designated by Jeffamine ED-2001[®] Fluka, average molecular weight 2001 g mol^{–1}) were dried under vacuum at 25 °C for several days prior to being used. 3-Isocyanatopropyltriethoxysilane (ICPTES, Fluka) was used as received. Ethanol (CH₃CH₂OH, Merck) and tetrahydrofuran (THF, Merck) were stored over molecular sieves. High purity distilled water (H₂O) was used in all experiments.

Preparation of the di-ureasil ormolytes

The KCF₃SO₃-doped POE/siloxane hybrids were prepared according to the synthetic procedure reported in detail elsewhere.^{23–25} The preliminary stage of the synthesis of the di-ureasils involved the formation of a covalent bond between the terminal NH₂ groups of Jeffamine-2001[®] ($a + c = 2.5$ and $b = 40.5$, Scheme 1) and the –N=C=O group of ICPTES in THF to yield the urea cross-linked organic–inorganic hybrid precursor designated as di-ureapropyltriethoxysilane (d-UPTES(2000)) (molar ratio Jeffamine 2001[®] : ICPTES = 1 : 2). The grafting process was infrared monitored. In the second stage of the synthetic procedure, a mixture of CH₃CH₂OH and water was added to the d-UPTES(2000) solution (molar ratio ICPTES : CH₃CH₂OH : H₂O = 1 : 4 : 1.5), followed by the incorporation of KCF₃SO₃. Samples with $n = \infty, 200, 100, 80, 60, 40, 20, 10, 7, 5$ and 1 were prepared. The structure of the d-U(2000)_nKCF₃SO₃ di-ureasils is depicted in Scheme 1. The samples with $n > 10$ were obtained as transparent and flexible monoliths. The d-U(2000)_nKCF₃SO₃ hybrids with $n = 7$ and 5 were produced as opaque films with a yellowish hue, whereas d-U(2000)₁KCF₃SO₃ is a white solid.

Preparation of the conductive oxide films

Transparent gallium-doped zinc oxide (ZnO–Ga) films were deposited on glass substrates by r.f. (13.56 MHz) magnetron sputtering using a ceramic oxide target (ZnO–Ga₂O₃ (95 : 5 wt%)); 5 cm diameter, supplied by SCM, Suffern, NY, USA). The sputtering process was carried out at room temperature, with an argon flow of 20 sccm (standard cubic centimetres per minute) and a deposition pressure of 0.11 Pa. The distance between the substrate and the target was 10 cm and the r.f. power density was maintained constant at 9 W cm^{–2}. Further

details of film preparation, as well as physical properties of the product, can be found in Assunção *et al.*²⁶

Preparation of the electrochromic films

Films of WO₃ were prepared by thermal evaporation using WO₃ pellets (SCM, 99.99% purity). The deposition pressure was 1.2×10^{-3} Pa with a deposition rate of 1.03 nm seg^{–1}.

Preparation of the ECD

Device assembly involved direct application of a small volume of the electrolyte sol to the surface of a 2.5×2.5 cm glass plate onto which a ZnO–Ga/WO₃ coating had been previously deposited. Two layers of sol were spread onto the substrates using a spinner (2000 rpm for 40 s). The thickness used for each layer was 200 nm for ZnO–Ga, and 300 nm for WO₃. A second glass plate coated with ZnO–Ga was placed on top of the ormolyte sample. The ECD built is represented in Scheme 2.

Techniques

²⁹Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra was recorded on a Bruker Avance 400 (9.4 T) spectrometer at 79.49 MHz with 2 μ s ($\theta \approx 30^\circ$) rf pulses, recycle delay of 60 s, and at a 5.0 kHz spinning rate. Chemical shifts (δ) are quoted in ppm from tetramethylsilane (TMS). The iterative least-squares curve-fitting procedure in the PeakFit software† was used to analyse the peaks observed in the ²⁹Si MAS NMR spectra quantitatively. The best fit of the experimental data was sought by varying the frequency, full-width-at-half-maximum and intensity of the peaks and by employing Voigt band shapes. The standard errors of the curve-fitting procedure were less than 0.01.

The X-ray diffraction (XRD) patterns were recorded at room temperature with a Rigaku Geigerflex D/max-c diffractometer system using monochromated CuK α radiation ($\lambda = 1.541$ Å) over the 2θ range of between 4 and 80°, and at a resolution of 0.05°. The samples were analysed as powders and were not subjected to any thermal pre-treatment.

The differential scanning calorimetry (DSC) measurements were obtained in a DSC131 Setaram. Disk sections with masses of approximately 20 mg were removed from the ormolyte, placed in 40 μ l aluminium cans and stored in a desiccator over phosphorous pentoxide for one week at room temperature under vacuum. After this drying treatment the cans were hermetically sealed and the thermograms were recorded. Each sample was heated from 25 to 300 °C at 10 °C min^{–1}. The purge gas used in all experiments was high purity nitrogen supplied at a constant 35 cm³ min^{–1} flow rate.

Samples for thermogravimetric analysis (TGA) studies were transferred to open platinum crucibles and analysed using a Rheometric Scientific TG 1000 thermobalance at a heating rate of 10 °C min^{–1} using dry nitrogen as purging gas (20 cm³ min^{–1}). Prior to measurement, the xerogels were vacuum-dried at 80 °C for about 48 h and stored in an argon-filled glovebox.

The total ionic conductivity of materials was determined by locating an ormolyte disk between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, >99.9%). Prior to characterisation, the di-ureasil ormolytes were vacuum-dried at 80 °C for about 48 h and stored in an argon-filled glovebox. The electrode–ormolyte–electrode assembly was secured in a suitable constant-volume support,²⁷ which was installed in a Buchi TO 51 tube oven. A calibrated type-K thermocouple, placed close to the ormolyte disk, was used to measure the sample temperature with a precision of about 0.2 °C and samples were characterised over a temperature range of between 25 and 100 °C. Bulk conductivities of the samples were obtained during heating cycles using the complex plane

† Jandel Corporation, 2591 Rerner Boulevard, San Rafael, CA 94901, USA

impedance technique (Schlumberger Solartron 1250 frequency response analyser and 1286 electrochemical interface) over a frequency range of 65 kHz to 0.5 Hz. The electrolyte behaviour was found to be almost ideal, and bulk conductivities were extracted in the conventional manner from impedance data. Reproducibility of measurements was better than 5%. In the case of the d-U(2000)₁KCF₃SO₃ ormolyte, conductivity values could not be measured below 75 °C, due to the high crystalline content of this sample and, consequently, its poor mechanical properties.

The electrochemical stability of electrolytes was evaluated within a dry argon-filled glovebox using a two-electrode cell configuration. Surface polishing of a 25 µm diameter gold microelectrode was completed outside the dry-box, and the electrode was washed and dried before transfer into the dry-box. Cell assembly was initiated by locating a clean lithium disk counter electrode (Aldrich, 99.9%, 10 mm diameter, 1 mm thick) on a stainless steel current collector. A sample of electrolyte was centred on the counter electrode and cell assembly was completed by supporting the microelectrode in the centre of the electrolyte disk using an appropriate clamp. An Autolab PGSTAT-12 (Eco Chemie) was used to record voltammograms at a scan rate of 100 mV s⁻¹. Measurements were conducted at room temperature within a Faraday cage located inside a glovebox.

The Fourier transform infrared (FT-IR) spectra were acquired at room temperature using a Bruker 22 (Vektor) spectrometer placed inside a glovebox with a dry argon atmosphere. The spectra were collected over the 4000–400 cm⁻¹ range by averaging 150 scans at a wavenumber resolution of 2 cm⁻¹. Solid samples (2 mg) were finely ground, mixed with approximately 175 mg of dried potassium bromide (KBr, Merck, spectroscopic grade) and pressed into pellets. Prior to recording the spectra, the pellets were vacuum dried at 80–90 °C for about 60 h, in order to reduce the levels of adsorbed water and solvent, and then transferred into a glovebox.

The Fourier transform Raman (FT-Raman) spectra were recorded with a resolution of 2 cm⁻¹ at room temperature with a Bruker IFS-66 spectrometer equipped with a FRA-106 Raman module and a near-infrared continuous YAG laser with wavelength of 1064 nm. The temperature stability in the sample was estimated to be ≈ 0.3 °C and during the measurements the sample cell was placed in an evacuated thermostat. The spectra were collected over the 3200–300 cm⁻¹ range at a resolution of 2 cm⁻¹. The accumulation time for each spectrum was 4 hours.

To evaluate complex FT-IR and FT-Raman band envelopes and to identify underlying spectral components, the iterative least-squares curve-fitting procedure in the PeakFit software† was used extensively. The best fit of the experimental data was obtained by varying the frequency, bandwidth and intensity of the bands. In the case of the disordered samples with $n \geq 40$ the peaks were fitted using a Gaussian function; for the more concentrated materials (which contain a crystalline POE-salt phase), we used a Voight function. A linear baseline correction with a tolerance of 0.2% was employed. The standard errors of the curve-fitting procedure were less than 0.003.

The room temperature optical reflectance spectra (380–850 nm) and the CIE (x,y) colour coordinates of the thin ECD were measured using a telescope optical probe (TOP 100 DTS140-111, Instrument Systems) coupled to a mini-array spectrometer (MAS40-100, Instrument Systems). The excitation source was a tungsten lamp (LS100-130, Instrument Systems) with a power supply (ES030-10, Elektronika) operating at 5.0 V. A standard aluminium mirror (Instrument Systems) was used as a reference reflectance sample. The experimental error is within 5%. The colouring and bleaching voltages were 4.0 V.

Results and discussion

Structure and morphology

The ²⁹Si MAS NMR spectra of the d-U(2000)_nKCF₃SO₃ ormolytes with $n = 80, 20$ and 7 are reproduced in Fig. 1. These samples give rise to three broad signals at $-53, -58$ and -66 ppm (Fig. 1), associated with T¹, T², and T³ units, on the basis of the conventional T^m₄ silicon (Si) notation (where $m = 1, 2$ and 3 represents the number of Si-bridging oxygen atoms). The relative population of the various Si sites in the three xerogels was estimated quantitatively through curve-fitting. At $n = 80$ the main site present is T³ [(SiO)₃SiR'] (60.6%), followed by the T² environment [(SiO)₂SiR'(OR)] (38.5%) and a minor concentration of the T¹ substructure [(SiO)SiR'(OR)₂] (0.9%), where R is H or CH₂CH₃ and R' represents the organic spacer (Scheme 1). This observation suggests that the condensation reactions favoured the growth of branched structures. In the more concentrated di-ureasil materials ($n = 20$ and 7) the T³ and T² substructures, clearly dominant, present similar concentrations ($\approx 48\%$). The degrees of polycondensation c (where $c = 1/3 (\%T^1 + 2\%T^2 + 3\%T^3)$) calculated for the three samples are: 87 % for d-U(2000)₈₀-KCF₃SO₃ and approximately 81 % for U(2000)₂₀KCF₃SO₃ and U(2000)₇KCF₃SO₃. These values are significantly higher than those of the non-doped matrix d-U(2000) (75%²⁸).

The XRD patterns of the KCF₃SO₃-doped di-ureasils with $100 \geq n \geq 20$, represented in Fig. 2, reveal that these samples are totally amorphous. These diffractograms exhibit a broad peak, Gaussian in shape, centered at ≈ 21.3 – 21.6° , ascribed to ordering within the siliceous network.²⁹ The structural unit distance, calculated using Bragg's law, is approximately 4.1–4.2 Å. The XRD patterns were fitted with pseudo-Voight functions with the purpose of determining the coherent length (L) over which the structural unit survives. A value for L of 10–12 Å was obtained, using the modified Scherrer equation $L = \lambda / (A \cos \theta)$, where I and A , in radians, are the maximum intensity and integrated area of the peaks, and λ is the wavelength of the radiation. The L values obtained for the K⁺-doped di-ureasils with $100 \geq n \geq 20$ are of the same order of magnitude of those found for non-doped di-ureasils.²⁹ In the XRD pattern of the d-U(2000)₂₀₀KCF₃SO₃ xerogel the pair of sharp and intense Bragg peaks observed at about 19.15 and 23.25° (Fig. 2) are indicative of the existence of crystalline POE domains.²⁹ At $n = 1$ a series of intense and sharp Bragg reflections also emerge (Fig. 2). While some of these peaks coincide with those of the pure salt ($n = 0$), other peaks are associated with the formation of a crystalline POE-KCF₃SO₃ complex.^{15,17,19} Based on previous studies,^{15,17} we conclude that the stoichiometry of this compound is 1 : 1. These results suggest that the d-U(2000)₁KCF₃SO₃ di-ureasil sample is essentially composed of the POE₁KCF₃SO₃ complex and a minor proportion of free triflate salt. No traces of POE were detected in the diffractogram of this salt-rich sample.

The DSC curves of the d-U(2000)_nKCF₃SO₃ hybrids with $40 \geq n \geq 7$ in the 20–300 °C range (Fig. 3(a)) demonstrate that these materials are amorphous. In the case of the KCF₃SO₃-doped di-ureasils with $200 \geq n \geq 60$, the weak endothermic peak observed at 33 °C (Fig. 3(a)) is associated with the fusion of POE crystallites. A single sharp, endothermic peak centred around 230 °C (onset at 220 °C) is seen in the thermogram of the most concentrated sample examined ($n = 1$) (Fig. 3(a)). Fig. 3(a) clearly demonstrates that this peak does not correspond solely to the fusion of pure KCF₃SO₃, which

† The typical notation T^m has been changed to T^m, to avoid any confusion with the notation n used for salt composition throughout the text.

melts at 241 °C (onset at 236 °C). This endotherm receives a major contribution from the melting peak of the POE₁KCF₃SO₃ complex^{15,17} and a minor contribution from the melting peak of the pure salt (Fig. 3(a)).^{15,17} As expected, the melting temperature of the POE₁KCF₃SO₃ complex formed within the d-U(2000) hybrid medium is considerably lower than that reported (260 °C¹⁷) for the POE₁KCF₃SO₃ complex derived from the linear high molecular weight POE used by Chintapalli *et al.*¹⁷

The d-U(2000)_nKCF₃SO₃ xerogels with $n > 40$ are thermally stable up to 310 °C (Fig. 3(b)). For $n = 40$ the slight, gradual mass loss that occurs from 156 to 390 °C, is followed by an abrupt mass loss (Fig. 3(b)). The TGA curves of the di-ureasils with $20 \geq n \geq 7$ display two thermal degradation processes: at 221 and 478 °C in the case of the sample with $n = 20$ and at 349, and 505/542 °C at $n = 10$ and 7 (Fig. 3(c)). Thermal degradation in the di-ureasil with $n = 1$ was observed in two stages: a slight, gradual mass loss takes place around 338 °C, followed by an abrupt change at 523 °C (Fig. 3(c)).

Ionic conductivity

Fig. 4 reproduces the Arrhenius conductivity plots of the d-U(2000)_nKCF₃SO₃ ormolytes with $\infty > n \geq 7$. Close analysis of these data reveal that the K⁺-doped di-ureasils with $n \geq 10$ display moderate to high levels of ionic conductivity within the whole range of temperatures considered, and demonstrate that the conductivity maximum is located at $n = 20$ (Fig. 4 and Table 1). At higher salt concentration ($n = 7$) the ionic conductivity suffers a marked reduction (Fig. 4). The ormolyte that displays the lowest ionic conductivity is the salt-rich hybrid with $n = 1$ (1.3×10^{-9} and 2.9×10^{-8} S cm⁻¹ at 80 and 100 °C, respectively) (not shown). This observation is consistent with the claim that a crystalline POE₁KCF₃SO₃ complex and free salt occur at the latter composition. In fact, Berthier *et al.*³⁰ demonstrated that the ionic conductivity in semi-crystalline polymer electrolytes is confined to the amorphous phase. In particular the formation of a crystalline POE-based compound (in the present case POE₁KCF₃SO₃) would be expected to restrict ion transport due to the immobilisation of the POE chains resulting from the complexation of the cations.³¹ These conclusions are in conflict with recent results of Gadjourouva *et al.*³² that suggest that ion transport in this sort of system may also occur in the crystalline region of the polymer network and, under certain circumstances, this contribution to the total conductivity may be greater than that of the amorphous component.

It is worth emphasizing that the data collected in Table 1 prove that the ionic conductivity exhibited by the d-U(2000)₂₀KCF₃SO₃ sample is significantly higher than that displayed by the conductivity maximum of the parent POE-based electrolyte system (POE₁₀KCF₃SO₃) and by the conductivity maxima of analogous long chain di-ureasil ormolytes doped with Li⁺, Mg²⁺ and Zn²⁺ ions.

Electrochemical stability

The electrochemical stability range of the KCF₃SO₃-doped POE-siloxane hybrids was determined by microelectrode cyclic voltammetry over the potential range between 0.0 and 7.0 V versus a lithium pseudo-reference electrode. The potential limit for the electrolyte system corresponds to the value at which a rapid rise in current was observed and where the current continued to increase as the potential was swept in the same direction. The overall stability of the electrolytes is excellent, with no electrochemical oxidation occurring at anodic potentials less than about 5.0 V. Fig. 5 shows the voltammogram obtained for the ormolyte sample that exhibits the highest conductivity ($n = 20$).

Spectroscopic study

The mechanism of ion conduction in the di-urea cross-linked POE-siloxane hybrid environment is expected to be different from that occurring in the classical POE-based medium.²⁰⁻²² While the POE host macromolecule possesses only one type of available coordinating site for the guest cations, (the ether oxygen atoms -COC-) the di-ureasil host network d-U(2000) provides, apart from the ether oxygen atoms of the short POE segments, the carbonyl oxygen atoms of the urea groups (-C=O). In both host media the cations may also interact with the triflate oxygen atoms (CF₃SO₃⁻). As a rule, the higher the ionic conductivity of an electrolyte, the higher the percentage of guest-salt dissociation. Cation-anion interactions give rise to the formation of associated ionic species (contact ion pairs and ionic multiplets) that lead to a reduction of the ionic conductivity.^{33,34}

To understand the mechanism of ion transport in the d-U(2000)_nKCF₃SO₃ hybrids, a FT-IR and FT-Raman spectroscopic study was carried out. The examination of some diagnostic bands of the polymer chains (CO stretching (νCO) and CH₂ rocking (τCH₂) modes), of the urea cross-links ("amide I" mode³⁵), and of the anion (SO₃ symmetric stretching (ν_sSO₃) mode), which suffer characteristic changes (intensity and/or frequency) upon cation coordination, will help us to elucidate the nature of the charge carriers present in the di-ureasil ormolytes.

K⁺-POE interaction: Fig. 6 shows the FT-IR spectra of selected K⁺-doped di-ureasils in the 1200-800 cm⁻¹ interval. The analysis of this range of wavenumbers is of interest because it is highly sensitive to alterations of the POE conformations arising from interactions of the ether oxygen atoms with the cations.

The νCO region (1200-1060 cm⁻¹) of the d-U(2000)_nKCF₃SO₃ samples with $n \geq 10$ displays an intense, broad band centred around 1110 cm⁻¹ and a shoulder at about 1147 cm⁻¹ (Fig. 6). These features, ascribed to the νCO vibration mode and to the coupled vibration of the νCO and rCH₂ modes, respectively,^{36,37a} are associated with non-coordinated, disordered POE chains.^{36,37a} In the K⁺-doped di-ureasils with $n = 5$ and 1, the single broad band at 1110 cm⁻¹ is replaced by two distinct, sharp peaks at 1115 and 1104 cm⁻¹ (Fig. 6). Both bands are indicative of the formation of the crystalline POE₁KCF₃SO₃ complex,¹⁷ thus confirming the conclusions retrieved from XRD and DSC. As the 1100 cm⁻¹ may be masked by these bands, the possibility that some POE chains remain amorphous and non-complexed cannot, however, be discarded.

The spectral interval 1000-800 cm⁻¹ of the FT-IR spectra shown in Fig. 6, the so-called rCH₂ region, comprises a mixture of rCH₂ and νCO modes.^{36,37} In this region the d-U(2000)_nKCF₃SO₃ samples with $n \geq 40$ produce two broad peaks centred at about 950 and 849 cm⁻¹, that are due to the coupled vibration of νCC/rCH₂ and νCO/rCH₂ modes, respectively.^{36,37} These data provide evidence that the conformations of the POE chains of d-U(2000) remain essentially unaffected in xerogels with $200 \geq n \geq 10$, and give support to the conclusion that the disordered polymer segments do not bond to the K⁺ ions in this range of salt content.^{36,37a} The profile of the rCH₂ region of the salt-rich samples with $n = 5$ and 1, however, differs dramatically from those of the more dilute xerogels: the band envelopes become significantly more intense and the band contours are more clearly defined (Fig. 6). The most important changes detected in the FT-IR spectra of this pair of highly concentrated di-ureasils are the development of two new, sharp bands at 936 and 893 cm⁻¹, and the downshift of the 849 cm⁻¹ event to 843 cm⁻¹ (Fig. 6). The 936, 893 and 843 cm⁻¹ bands represent unequivocal proof of the formation of the crystalline POE₁KCF₃SO₃ compound.¹⁷ In

particular the feature at 843 cm^{-1} suggests that, as expected, the $\text{O}-\text{C}-\text{O}$ torsional angle in this complex is close to that of non-complexed, crystalline POE chains,^{37b} organised along a helical-like structure (*gauche* conformations).

K⁺-urea cross-link interaction: The “amide I” mode of the di-ureasils^{24,25,38,39} is a very complex vibration that receives a major contribution from the $\text{C}=\text{O}$ stretching vibration. In general, this band consists of several distinct components that correspond to different $\text{C}=\text{O}$ environments designated as associations, aggregates or structures.

The “amide I” region ($1800\text{--}1600\text{ cm}^{-1}$) of selected d-U(2000)_nKCF₃SO₃ di-ureasils and the results of the curve-fitting performed with selected representative samples are represented in Fig. 7(a) and 7(b), respectively.

The “amide I” band of the K⁺-doped di-ureasils with $n \geq 10$ was resolved into five individual components situated at approximately 1751 , 1720 , 1682 , 1660 and 1642 cm^{-1} (Fig. 7(b)). The band at 1751 cm^{-1} is associated with the absorption of urea groups in which the N-H or C=O groups are free from any interaction.^{24,25,38,39} The bands near 1720 , 1682 and 1661 cm^{-1} are ascribed to the absorption of hydrogen-bonded C=O groups of disordered hydrogen-bonded POE-urea associations of increasing strength.^{24,25,38,39} Finally, the 1640 cm^{-1} feature is assigned to the absorption of C=O groups included in significantly more ordered hydrogen-bonded urea-urea associations.^{24,25,38,39}

Comparison of the profile of the “amide I” band of the d-U(2000)_nKCF₃SO₃ di-ureasils with $n = 200$, 80 and 40 with that of the non-doped host matrix allows us to conclude immediately that they are very similar (Fig. 7(a)). Fig. 7(b) demonstrates that the intensity of the “amide I” components of d-U(2000) does not suffer significant changes with the increase of salt content in hybrids with $n > 20$. These findings mean that the associations formed in d-U(2000) are only slightly perturbed by the presence of the guest salt in this range of salt composition and that, as a consequence, the strength of hydrogen bonds remains essentially the same.

Fig. 7(a) reveals that in the low frequency side of the “amide I” region of the material with $n = 20$, a broad, strong envelope centred at approximately 1675 cm^{-1} and displaying a shoulder at 1646 cm^{-1} emerges. Fig. 7(b) shows that at this composition the intensity of the 1750 and 1720 cm^{-1} peaks is slightly reduced, whereas that of the 1680 , 1660 and 1641 cm^{-1} bands is significantly enhanced.

At even higher salt concentration ($n = 10$), the component characteristic of “free” C=O groups (1750 cm^{-1}) disappears (Fig. 7(b)), indicating that the urea cross-links become saturated at this salt content. At the same time, while some disordered POE-urea associations (1720 cm^{-1}) are disrupted, more ordered POE-urea aggregates (1680 , 1660 and 1641 cm^{-1}) are formed (Fig. 7(b)).

Globally we may deduce from the analysis of the “amide I” region of the K⁺-doped di-ureasils that the dominant hydrogen-bonded associations formed at $n \leq 20$ are the three most ordered and thus strongest associations of d-U(2000) that exist in a minor proportion. It is very likely that these associations formed at high salt content include carbonyl groups bonded to K⁺ ions.

Cation-anion interaction: The non-degenerate $\nu_3\text{SO}_3$ mode of the CF_3SO_3^- ion is a powerful tool that may be used to evaluate ionic association. The $\nu_3\text{SO}_3$ band of a “free” triflate ion was located at 1032 cm^{-1} .⁴⁰ Upon coordination to the K⁺ ion, the $\nu_3\text{SO}_3$ is shifted to higher wavenumbers.¹⁷

The FT-IR and FT-Raman spectra of selected d-U(2000)_nKCF₃SO₃ di-ureasils in the $\nu_3\text{SO}_3$ region are represented in Fig. 6 and Fig. 8, respectively. The results of the curve fitting performed in the FT-IR and FT-Raman $\nu_3\text{SO}_3$ band of representative xerogels are depicted in Fig. 9(a) and 9(b), respectively.

The intensity maximum of the FT-IR and FT-Raman $\nu_3\text{SO}_3$ envelope of the K⁺-doped hybrids with $n \geq 10$ is seen at 1032 cm^{-1} (Fig. 6 and Fig. 8, respectively). In the case of the

d-U(2000)_nKCF₃SO₃ compound, the FT-IR and FT-Raman $\nu_3\text{SO}_3$ intensity maxima are located at 1038 cm^{-1} (Fig. 6) and at 1047 cm^{-1} (Fig. 8), respectively.

The FT-IR (Fig. 9(a)) and FT-Raman (Fig. 9(b)) $\nu_3\text{SO}_3$ mode of the samples with $n \geq 10$ was decomposed into three individual components: a band at $1032/1031\text{ cm}^{-1}$ and two weak shoulders at $1039/1038$ and 1026 cm^{-1} . In the FT-IR $\nu_3\text{SO}_3$ region of the salt-rich ormolytes with $n = 5$ and 1 (Fig. 9(a)), the 1039 cm^{-1} band becomes the dominant event and three new components (shoulders) emerge at 1056 , 1045 and 1017 cm^{-1} . In the FT-Raman $\nu_3\text{SO}_3$ spectra of the d-U(2000)_nKCF₃SO₃ and d-U(2000)_nKCF₃SO₃ composites (Fig. 9(b)), the intensity of the bands detected in the more dilute hybrids drops drastically and three new events appear: a strong band at 1047 cm^{-1} and two shoulders at 1050 and 1035 cm^{-1} .

The $\nu_3\text{SO}_3$ band at 1032 cm^{-1} , present in the FT-IR and FT-Raman spectra of all the materials examined here, is assigned to “free” ions.⁴⁰ Nevertheless, this band can also be associated with the existence of “cross-link-separated ion pairs”.⁴¹ This could explain the regular increase of the intensity of this feature as more KCF₃SO₃ is progressively incorporated and also its remarkable intensity in the FT-IR spectrum of the di-ureasil with $n = 1$.

The shoulders at 1026 and $1039/1038\text{ cm}^{-1}$ observed in FT-IR (Fig. 9(a)) and FT-Raman (Fig. 9(b)) spectra of the doped d-U(2000) based hybrids are associated with weakly coordinated triflate ions located in two different sites:⁴¹ (1) CF_3SO_3^- species weakly bonded to K⁺ ions, which simultaneously interact with the carbonyl oxygen atoms of the urea groups; (2) CF_3SO_3^- ions hydrogen-bonded to the urea N-H groups.

The event at $1045/1047\text{ cm}^{-1}$ in the FT-IR (Fig. 9(a)) and FT-Raman (Fig. 9(b)) spectra of the more concentrated samples ($n = 7$, 5 and 1) is tentatively ascribed to contact ion-pairs.

The bands at 1056 and 1017 cm^{-1} that appear in the FT-IR spectra (Fig. 9(a)) of the di-ureasils with $n = 5$ and 1 must be due to the formation of higher ionic aggregates. In principle, the vibration involved in both modes does not imply a change in the polarisability of the species in question, since this pair of bands has no counterpart in the FT-Raman spectra (Fig. 8 and Fig. 9(b)).

The weak 1050 and 1035 cm^{-1} features seen in the FT-Raman spectrum of the most concentrated xerogel (Fig. 9(b)) support the presence of a minor proportion of free crystalline KCF₃SO₃,⁴² thus corroborating the above XRD interpretation.

The main conclusion that stems from the spectroscopic study performed in the present section is that, in accordance with the situation found in analogue long-chain di-ureasil systems^{23–25} the charge carriers of the conductivity maximum d-U(2000)₂₀KCF₃SO₃ are “free” anions or weakly coordinated species.

Electrochromic device performance

To be used in an optical device a polymer electrolyte film must meet various pre-requisites. One of these is that the film must exhibit high transmission. If this condition is not fulfilled the electrolyte will have an adverse influence on colour contrast.⁴³

Fig. 10 shows the optical reflectance spectra in the wavelength range between 380 and 810 nm for a prototype ECD based on the d-U(2000)₂₀KCF₃SO₃ di-ureasil. The use of this sample (conductivity maximum of this di-ureasil system) led to the best results. The average transmittance in the visible region is situated at $85\text{--}95\%$ for the bleached state (Fig. 10). The bleaching/colouring time was approximately 60 s . The transmittance of the coloured state is $\sim 90\%$, showing a peak value at 638 nm .

The change in colour from the bleached to the coloured state was quantitatively evaluated by the estimation of the colour coordinates, according to the standard methods proposed by the Commission Internationale d'Eclairage (CIE), using the 2° observer. As shown in the (x,y) CIE diagram in Fig. 11, from

the bleached to the coloured state the ECD changes from the yellow (0.38,0.37) to the blue (0.29,0.29) spectral region. The colour change is reversible. The ECDs tested exhibit good electrochemical stability, show memory effect and may therefore be of interest for application in "smart windows".

Conclusions

We have demonstrated that the combination of the hybrid and sol-gel strategies for the modification of the POE architecture and the creation of a di-urea cross-linked POE-siloxane (di-ureasil) network represents a viable and successful alternative in the case of electrolyte systems doped with KCF_3SO_3 , as the ionic conductivities obtained here are higher than those reported for the conventional POE-based electrolytes.

Moreover, the encouraging results observed in this study of KCF_3SO_3 -doped POE-siloxane ormolytes confirm the advantages that derive from the use of di-ureasil matrices in ECDs. Clearly further optimisation of the procedures (e.g., the use of a counter electrode based on NiO and the application of an appropriate sealant to avoid electrolyte degradation) is required, and improvements in device response time, optical transmittance and memory effect under open circuit voltages may be expected.

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Scheme 1 Structure of the d-U(2000)_nKCF₃SO₃ di-ureasils.

Scheme 2 Construction of the electrochromic device (a), and view of the coloured state (b)

Fig. 1 ²⁹Si MAS NMR spectra of selected d-U(2000)_nKCF₃SO₃ di-ureasils

Fig. 2 XRD patterns of selected d-U(2000)_nKCF₃SO₃ di-ureasils.

Fig. 3 (a) DSC curves of the d-U(2000)_nKCF₃SO₃ di-ureasils, (b) and (c) TGA curves of selected d-U(2000)_nKCF₃SO₃ di-ureasils

Fig. 4 Arrhenius conductivity plot of the d-U(2000)_nKCF₃SO₃ di-ureasils.

Table 1 Conductivity maxima of polymer electrolyte systems incorporating alkaline, alkaline-earth and transition metal triflate salts

System	Ionic conductivity/S cm ⁻¹		Ref.
	<i>T</i> = 22 °C	<i>T</i> = 100 °C	
POE ₁₀ KCF ₃ SO ₃	9.3×10^{-6}	4.5×10^{-4}	17
d-U(2000) ₂₀ KCF ₃ SO ₃	1.1×10^{-5}	6.2×10^{-4}	This work
d-U(2000) _{20/10} LiCF ₃ SO ₃	2.8×10^{-6} (<i>n</i> = 20)	2.1×10^{-4} (<i>n</i> = 10)	23
d-U(2000) ₂₀ Mg(CF ₃ SO ₃) ₂	4.0×10^{-6}	6.7×10^{-5}	24
d-U(2000) _{60/20} Zn(CF ₃ SO ₃) ₂	5.8×10^{-6} (<i>n</i> = 60)	7.3×10^{-5} (<i>n</i> = 20)	25

Fig. 5 Room temperature cyclic voltammogram of the d-U(2000)₂₀-KCF₃SO₃ di-ureasil obtained with a gold microelectrode and lithium counter/reference electrode (sweep rate 100 mV s⁻¹).

Fig. 6 FT-IR spectra of selected d-U(2000)_nKCF₃SO₃ di-ureasils in the 1200–800 cm⁻¹ region (νCO, νCH₂ and νSO₃ envelopes). The frequencies indicated represent the average value of the frequencies of all the samples considered.

Fig. 7 (a) FT-IR spectra of selected d-U(2000)_nKCF₃SO₃ di-ureasils in the "amide I" region, and (b) curve-fitting results. The frequencies indicated represent the average value of the frequencies of all the samples considered.

Fig. 8 FT-Raman spectra of selected d-U(2000)_nKCF₃SO₃ di-ureasils in the ν_3 SO₃ region. In order to examine exclusively the contribution of the ν_3 SO₃ mode, the FT-Raman spectrum of the pure polymer had to be first subtracted from those of the hybrids with $n \geq 7$. The frequencies indicated represent the average value of the frequencies of all the samples considered.

Fig. 9 Curve-fitting results of selected d-U(2000)_nKCF₃SO₃ di-ureasils in (a) the FT-IR, and (b) FT-Raman ν_3 SO₃ regions. The frequencies indicated represent the average value of the frequencies of all the samples considered.

Fig. 10 Optical reflectance spectra for the ECD structure using $\text{U}(2000)_{20}\text{KCF}_3\text{SO}_3$ as ormolyte in (1) bleached, and (2) coloured states.

Fig. 11 CIE chromaticity diagram (1931) showing the (x,y) colour coordinates of the ECD structure using $\text{U}(2000)_{20}\text{KCF}_3\text{SO}_3$ as ormolyte in bleached and coloured states.