Sol-gel-derived potassium-based di-ureasils for “smart windows”

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Sol-gel-derived KCF$_2$SO$_4$-doped di-urea cross-linked poly(ethylene) (POE)siloxane (di-urea) ormylotes with \( n > 1 \) (\( n \) is the number of oxyethylene units per K$^+$ ion) have been analysed. Samples with \( n > 40 \) are thermally stable up to 310°C. At \( n < 100 \), POE crystals are present. At \( n = 5 \), a crystalline POE-KCF$_2$SO$_4$ complex with stoichiometry 1:1 is formed. In the aerogel 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” amine and weakly coordinated CF$_3$SO$_3$ 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 carbonates by POE occurs at \( n < 20 \). In the latter composition range, contact ion pairs and higher ionic aggregates develop. The ormylotes were successfully used in the assembly of prototype electrochromic devices (ECDs) that exhibit good chemical stability and demonstrate a memory effect. The ECD incorporating the ormylote with \( n = 20 \) displays an average transmittance in the visible region of \( 98\% \) in the coloured state and of \( 85-85\% \) in the bleached state. The corresponding change in colour, evaluated on the basis of the Commission Internationale d’Eclairage (CIE) colour-coordinates system, is reversible; from yellow (0.38, 0.37) to: 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 control and display of optical information, anti-glare automotive rear- and side-view mirrors, sunglasses, protective eyewear for military use, aircraft windows with controllable optical transmission, glare-reduction systems for buildings or “smart windows”, and reactive labels.2,3

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 electrically conducting oxide film (e.g., tin-doped indium oxide (ITO)2 or gallium-doped zinc oxide (GZO)-Co$_3$O$_4$-coated glass (or plastic) sheet).4

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-rate 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. Tungsten trioxide (WO$_3$), by far the most widely studied electrochromic material, undergoes reversible optical switching from whitish yellow to dark blue, as a result of an electrochemical process based on simultaneous injection and extraction of electrons and ions (double injection).5

In recent years the sol-gel method6 has become a popular way for producing ECDs.7 This versatile synthetic route is advantageously applied to the preparation of high quality electrochromic coatings. Some organo-inorganic sol-gel-derived hybrid materials8 have also been proposed as electrolys in ECDs.9,10 With respect to classical polymer electrolytes, organics (acrylonitrile-modified siloxanes) offer a series of benefits, in particular an essentially amorphous character, high transparency, better mechanical resistances, improved chemical/stability and the ability to solubilise greater quantities of guest salts, avoiding phase separation or “salt-out-out.”

The high ionic conductivity exhibited by polymer electrolyte systems (conventional or hybrid) incorporating K$^+$ ion9,10 prompted us to investigate in the present work the morphology, structure, thermal properties, ionic conductivity and ionic...
electrolytes in ECDs. With respect to classical polymer electrolytes, 14 ormosilates (aerosol of organically modified silazane 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 "salt-out-out".

The high ionic conductivity exhibited by polymer electrolyte systems (conventional or hybrid) incorporating K+ ions15,18 prompted us to investigate in the present work the morphology, structure, thermal properties, ionic conductivity and ionic association of a family of potassium trifluoromaleate (KCF3SO3)-based poly(vinylidene difluoride) (POVDF)/polyvinylidene fluoride (PVDF) blends with potential application as ionicomers in the fabrication of "smart windows". The host hybrid framework employed, designated as d-UV(2000), belongs to the class of dia-ureasil-silicas,25-27 a series of hybrid networks in which the organic and inorganic components are bonded through siloxane groups. The sample with the highest ionic conductivity has been applied in the fabrication of a glass/ZnO-Ga/Ga II(0001)/KCF3SO3-Nb2O5/ZnO-Ga-Ga II GaAs ECD.

**Experimental**

**Materials**

Potassium trifluoromaleate (KCF3SO3, Aldrich) and α,α,α-trimethoxysilane (ATMS, Aldrich) (commercially designated by Jeﬀamine ED-2000)16 (Fluka, average molecular weight 2001 g mol−1) were dried under vacuum at 25 °C for several days prior to being used. 3-Hexyltrimethoxysilane (HTMS, Aldrich) (commercially designated by Jeﬀamine ED-2000)16 (Fluka, average molecular weight 2001 g mol−1) were dried under vacuum at 25 °C for several days prior to being used. 3-Hexyltrimethoxysilane (HTMS, Aldrich) (commercially designated by Jeﬀamine ED-2000)16 (Fluka, average molecular weight 2001 g mol−1) were dried under vacuum at 25 °C for several days prior to being used.

**Preparation of the dia-ureasil ionicomers**

The KCF3SO3-doped POE/ilsaionite hybrids were prepared according to the synthetic procedure reported elsewhere.25,27 The preliminary stage of the synthesis of the dia-ureasil involved the formation of a covalent bond between the terminal NH2 groups of Jeﬀamine ED-2000 (α = 2.3 and n = 40.5, Scheme 1) and the C=O group of ICTES (Fluka) with a carboxylated organic-inorganic hybrid precursor designated as d-ureasil(ureasil) (d-UPTES)(2000) solution (molar ratio ICTES: CH3OH: H2O: 1: 4: 1: 5), followed by the incorporation of KCF3SO3, Samples with α = 200, 100, 10, 5, 1, 7, 5 and 1 were prepared. The structure of the d-UV(2000)/KCF3SO3 dia-ureasil is depicted in Scheme 1. The samples with α > 10 were obtained as transparent and flexible membranes. The d-UV(2000)/KCF3SO3 hybrids with α = 7 and 5 were produced as opaque films with a yellowish hue, whereas d-UV(2000)/KCF3SO3 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 w%), 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 centimeters 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 Assmann et al.26

Preparation of the electrochromic film

Fils of WO3 were prepared by thermal evaporation using WO3 pellets (SCM, 99.999% purity). The deposition pressure was 1.2 × 10−3 Pa with a deposition rate of 1.63 nm s−1. WO3 film was 20 nm thick and deposited on both sides of the dielectric films. The WO3 films were then annealed at 100 °C for 2 hours. The films were then used to fabricate the ECDs.

Preparation of the ECD

Device assembly involved direct application of a small volume of the electrochromic oxide on the surface of a 2.5 × 2.5 cm glass plate onto which a ZnO-Ga-WO3 composite film was previously deposited. Two layers of silver were spread onto the substrates using a spinner (2000 rpm for 40 s). The thickness used for each layer was 150 nm and for ZnO-Ga and WO3. A second glass plate coated with ZnO-Ga was placed on top of the oxide sample. The ECD built is represented in Scheme 2.

**Techniques**

The X-ray diffraction (XRD) patterns were recorded at room temperature with a Rigaku Geigerflex D/Max diffractometer using monochromated CuKα radiation (λ = 1.541 Å) over the 2θ range of between 40 and 80° and at a resolution of 0.05°. The samples were analyzed as powders and were not subjected to any thermal pretreatment. The differential scanning calorimetry (DSC) measurements were obtained in a DSC-131 Netzsch device with a heating rate of 5 °C min−1.

The total ionic conductivity of materials was determined by locating an ormosil disk between two 10 cm diameter iron-blocking gold electrodes (Goodfellow, >99.9%). Prior to characterization, the dia-ureasil ionicomers were vacuum-dried at 80 °C for about 48 h and stored in an argon-filled glovebox. The electrode-ormosil-electrode assembly was secured in a suitable constant-volume support,27 which was installed in a Buchi T151 tube oven. A calibrated type-K thermocouple, placed close to the ormosil disk, was used to measure the sample temperature with a precision of about 0.2 °C and samples were characterized over a temperature range of between 23 and 100 °C. Bulk conductivities of the samples were obtained during heating cycles using the complex plane
impedance technique (Schnabelberger Solution 1250 frequency response analyzer and 1256 electrochemical interface) over a frequency range of 55 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)KCF$_2$SO$_4$-3 wt% KCl, the peak heights in the cyclic voltammetry were recorded after 30 min at 18°C, due to the highly crystalline nature 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 25 mm diameter gold microelectrode was carried out inside 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 coated 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 IFS-66 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 dry 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 min 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 3200-1800 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 doped samples with n ≥ 40 the peaks were fitted using a Gaussian function; for the more concentrated materials (which contain a crystalline PO$_4$-salt phase), we used a Voigt 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 (380–550 nm) and the CH$_3$(H$_2$O) colour coordinates of the thin ECD overlays were measured using a UV/visible optical probe (TOP 106 DTS410-111, Instrument Systems) coupled to a mini-cuvette spectrometer (MAS400-100, Instrument Systems). The excitation source was a tungsten lamp (LS400-130, Instrument Systems) with a power supply (BSG00-10, Electrostar) operating at 50 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 4.6 V.

Results and discussion
Structure and morphology
The 85Si MAS NMR spectra of the d-U(2000)KCF$_2$SO$_4$-3 wt% KCl with n = 10, 20 and 7 are reproduced in Fig. 1. These samples give rise to three broad signals at -33, -55 and -66 ppm (Fig. 1), associated with T$^\ddagger$, T$^\ddagger$, and T$^\ddagger$ units, on the basis of the conventional 0° 7 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 = 60 the main site present is T$^\ddagger$(Si(SiO$_4$)Si($\ddagger$)) (46.6%), followed by the T$^\ddagger$ environment [Si($\ddagger$)Si($\ddagger$)O($\ddagger$)] (38.5%) and a minor concentration of the T$^\ddagger$ substructure [Si($\ddagger$)Si($\ddagger$)O($\ddagger$)] (9.0%), where R is H or CH$_3$ and R$^\ddagger$ represents the organic spacer (Scheme I). This observation suggests that the condensation reactions favoured the growth of branched structures. In the more concentrated d-$^3$-ureasils (n = 20 and 7) the T$^\ddagger$ and T$^\ddagger$ substructures, clearly dominant, present similar concentrations (±4%). The degree of polymerisation $\bar{p}$ (where $\bar{p}$ = $\Sigma$ $n_i$ $\bar{p}_i$) calculated for the three samples are: 87% for d-U(2000)KCF$_2$SO$_4$ and approximately 81% for d-U(2000)KCF$_2$SO$_4$ and d-U(2000)KCF$_2$SO$_4$. These values are significantly higher than those of the non-doped matrix d-U(2000)KCF$_2$SO$_4$ (75%).

The XRD patterns of the KCF$_2$SO$_4$-doped d-ureasils with n ≥ 20, represented in Fig. 2, reveal that these samples are totally amorphous. These diffractionograms exhibit a broad peak, Gaussians in shape, centered at 2θ = 21.2–21.6°, assigned to ordering within the siliceous network. The structural unit distance, calculated using Bragg’s law, is approximately 4.0 ± 0.2 Å. The XRD patterns were fitted with pseudo-Voigt functions with the purpose of determining the coherent length (L) over which the structural unit survives. A value for L of 12.1–12.9 Å was obtained, using the modified Scherrer equation $L = k D \cos \theta / \beta$, where k and $\lambda$ are the maximum intensity and integrated area of the peaks, and $\beta$ is the wavelength of the radiation. The L values obtained for the K$_2$-doped d-ureasils with n ≥ 20 are the same order of magnitude as those found for non-doped d-ureasils. These data suggest that the d(U(2000)KCF$_2$SO$_4$-3 wt% KCl) sample with n ≥ 20 shows 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 PO$_4$-KCF$_2$SO$_4$ complex. Based on previous studies, 11,12 we conclude that the stoichiometry of this compound is 1:1. These results suggest that the d(U(2000)KCF$_2$SO$_4$-3 wt% KCl) sample is essentially composed of the PO$_4$-KCF$_2$SO$_4$ complex and a minor proportion of the pure salt. No traces of PO$_4$ were detected in the diffractogram of this salt-rich sample.

The DSC curves of the d(U(2000)KCF$_2$SO$_4$-3 wt% KCl) hybrids with n > 20 in the 60–300°C range (Fig. 3a) demonstrate that these materials are amorphous. In the case of the KCF$_2$SO$_4$-doped d-ureasils with n ≥ 20, the weak exothermic peak observed at 33°C (Fig. 3a) is associated with the fusion of PO$_4$ crystallites. A single, broad exothermic peak centered around 230°C (onset at 220°C) is seen in the thermogram of the most concentrated sample examined (n = 7) (Fig. 3a). These results clearly demonstrate that this peak does not correspond solely to the fusion of pure KCF$_2$SO$_4$, which

1. The typical notation T$^\ddagger$ has been changed to T$^\ddagger$, to avoid any confusion with the notation used for salt composition throughout the text.
mells at 241 °C (onset at 235 °C). This exotherm receives a major contribution from the melting peak of the POE-KCF₃SO₃ complex, and a minor contribution from the melting peak of the pure salt (Fig. 3(a)).

As expected, the melting temperature of the POE-KCF₃SO₃ complex formed within the d-U(2000) hybrid medium is considerably lower than that reported (260 °C) for the POE-KCF₃SO₃ complex derived from the linear high molecular weight POE used by Chintapalli et al. The d-U(2000) KCF₃SO₃ 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 290 °C is followed by an abrupt mass loss (Fig. 3(b)). The TGA curves of the di-ureasils with n = 20 and n = 35 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 n = 10 and 7 (Fig. 3(c)). Thermal degradation in the di-ureasils 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) KCF₃SO₃ xerogels with n > n ≥ 7. Close analysis of these data reveals that the K⁺ doped di-ureasil with n = 10 displays moderate to high levels of ionic conductivity within the whole range of temperatures considered, and demonstrates that the conductivity maximum is located at n = 20 (Fig. 4 and Table 1). At higher salt concentrations (n = 7 the ionic conductivity suffers a marked reduction (Fig. 4). The ionic conductivity of the salt-rich hybrid with n = 1 (1.3 × 10⁻⁹ and 2.9 × 10⁻⁷ S cm⁻¹ at 80 and 100 °C, respectively) is similar to that at the latter composition. In fact, Berthier et al. demonstrated that the ionic conductivity in semi-crystalline polymeric electrolytes is essentially determined by the amorphous phase. In particular, the formation of a crystalline POE-based compound (in the present case POE-KCF₃SO₃) would be expected to restrict ion transport due to the immobilization of the POE chains resulting from the crystallization of the cations. These conclusions are in conflict with recent results of Gudzenkova et al. 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) KCF₃SO₃ samples is significantly higher than that displayed by the conductivity maximum of the parent POE-based electrolyte system (POE-KCF₃SO₃) and by the conductivity maxima of analogous long chain di-ureasil xerogels doped with Li⁺, Mg²⁺ and Zn²⁺ ions.

### Electrochemical stability

The electrochemical stability range of the KCF₃SO₃-doped POE-ureasil xerogel 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 electrolyte sample that exhibits the highest conductivity (n = 20).

### Spectroscopic study

The mechanism of ion conduction in the di-ureasil cross-linked POE-clay hybrids is expected to be different from that occurring in the classical POE-based medium. While the POE host macromolecule contains only one type of available coordinating site (the guest cations, the ether oxygen atoms -CO-) 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 (anion dimers and ionic multimers) that lead to a reduction of the ionic conductivity. To understand the mechanism of ion transport in the d-U(2000)KCF₃SO₃ hybrids, a FT-IR and FT-Raman spectroscopic study was carried out. The examination of some diagnostic bands of the polymer chains (C=O stretching (νCO) and C-H rocking (νCH₂) modes) of the urea cross-links (inside 1st mode) and of the anion (SO₃ symmetric stretching (νSO₃) 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 xerogels.

K⁺-POE interaction: Fig. 6 shows the FT-IR spectra of selected K⁺-doped di-ureasils in the 1280–800 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 other oxygen atoms with the cations. The νCO region (1200–1060 cm⁻¹) of the d-U(2000) KCF₃SO₃ samples with n > 10 displays an intense, broad band centred around 1110 cm⁻¹ and a shoulder at about 1147 cm⁻¹ (Fig. 6). These features, attributed to the νCO vibration mode and to the coupled vibration of the νCO and νCH₂ modes, respectively, are associated with non-coordinated, disordered POE chains. In the K⁺-doped di-ureasils with n = 5 and 1, the single broad band at 1140 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 POE-KCF₃SO₃ complex, thus confirming the conclusions retrieved from XRD and DSC. The 1109 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 1009–800 cm⁻¹ of the FT-IR spectra shown in Fig. 6, the so-called νC-H region, comprises a mixture of νCH₂ and νCO modes. In this region the d-U(2000) KCF₃SO₃ samples with n > 40 produce two broad peaks centred at about 990 and 849 cm⁻¹, that are due to the coupled vibration of νCO+CH₂ and νCO+CH₃ modes, respectively. These data provide evidence that the conformations of the POE chains of d-U(2000) remain essentially unaffected in xerogels with 20 > n > 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. The νCH₂ 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 POE-KCF₃SO₃ compound. In
particular the feature at 843 cm\(^{-1}\) suggests that, as expected, the O-C-O-C-O torsional angle in this complex is close to that of non-complexed, crystalline POI chains, organized along a helix-like structure (gauche conformations).

*K*-area cross-link interaction: The "amide I" mode of the d-\(\text{U}(2000)_{\text{k}}\) complex is a very complex vibration that receives a major contribution from the C-O stretching vibration. In general, this band consists of several distinct components that correspond to different C-O environments designated as associations, aggregates or structures.

The "amide I" band of the K*-doped d-\(\text{U}(2000)_{\text{k}}\) is associated with the absorption of urea groups in which the N-H or C-O groups are free from any interaction.\(^{33,32,33}\) The bands near 1720, 1662 and 1641 cm\(^{-1}\) are assigned to the absorption of hydrogen-bonded C-O groups of disordered hydrogen-bonded POE-urea associations of increasing strength.\(^{32,38,39}\) Finally, the 1640 cm\(^{-1}\) band is assigned to the absorption of C-O groups included in significantly more ordered hydrogen-bonded urea-urea associations.\(^{34,35,38,39}\)

Comparison of the profile of the "amide I" band of the d-\(\text{U}(2000)_{\text{k}}\) and d-\(\text{U}(2000)_{\text{k}}\) systems 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-\(\text{U}(2000)_{\text{k}}\) does not suffer significant changes with the increase of salt content in the N-III group. These findings mean that the associations formed in d-\(\text{U}(2000)_{\text{k}}\) 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.

At even higher salt concentrations (c = 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 higher cation content. At the same time, some other 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)).

We may deduce from the analysis of the "amide I" region of the K*-doped d-\(\text{U}(2000)_{\text{k}}\) that the dominating hydrogen-bonded associations formed at c ≤ 20 are the three most ordered and thus strongest associations of d-\(\text{U}(2000)_{\text{k}}\) 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-ion interaction: The non-degenerate v\(_{\text{SO}}\) mode of the CTF\(_{\text{SO}}\) ion is a powerful tool that may be used to evaluate ionic association. The v\(_{\text{SO}}\) band of a "free" triflate ion was located at 1032 cm\(^{-1}\).\(^{40}\) Upon coordination to the K*-ion, the v\(_{\text{SO}}\) is shifted to higher wavenumbers.\(^{41}\) The FT-IR and FT-Raman spectra of selected d-\(\text{U}(2000)_{\text{k}}\) complexes of representative xerogels are depicted in Fig. 9(a) and 9(b), respectively.

The intensity maximum of the FT-IR and FT-Raman v\(_{\text{SO}}\) envelope of the K*-doped hybrids with c ≥ 10 is seen at 1032 cm\(^{-1}\) (Fig. 6 and Fig. 8, respectively). In the case of the d-\(\text{U}(2000)_{\text{k}}\) complex, the FT-IR and FT-Raman v\(_{\text{SO}}\) line 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)) v\(_{\text{SO}}\) mode of the samples with c ≥ 10 was decomposed into three individual components: a band at 1032/1031 cm\(^{-1}\) and two weak shoulders at 1039/1038 and 1026 cm\(^{-1}\). In the FT-IR c-\(\text{SO}_{\text{III}}\) region of the salt-rich xerogels with c = 5 and 1 (Fig. 9(a)), the 1039 cm\(^{-1}\) band becomes the dominant event and these new components (shoulders) emerge at 1056, 1045 and 1017 cm\(^{-1}\). In the FT-Raman v\(_{\text{SO}}\) spectra of the d-\(\text{U}(2000)_{\text{k}}\) complexes (Fig. 9(b)), the intensity of the bands detected in the more dilute hybrids drops drastically and these new events appear: a strong band at 1047 cm\(^{-1}\) and two shoulders at 1050 and 1035 cm\(^{-1}\).

The v\(_{\text{SO}}\) band at 1032 cm\(^{-1}\) is 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-links-separated ion pairs".\(^{42}\) This could explain the regular increase of the intensity of this feature as more KCTF\(_{\text{SO}}\) is progressively incorporated and also its remarkable intensity in the FT-IR spectrum of the d-\(\text{U}(2000)_{\text{k}}\) complex with c ≥ 10.

The shoulders at 1050 and 1035 cm\(^{-1}\) are observed (Fig. 9(a)) and FT-Raman (Fig. 9(b)) spectra of the d-\(\text{U}(2000)_{\text{k}}\) based hybrids are associated with weakly coordinated triflate ions located in two different sites: (1) CF\(_{3}\)SO\(_{3}\) ions weakly bonded to K*-ions which simultaneously interact with the carbonyl oxygen atoms of the urea groups; (2) CF\(_{3}\)SO\(_{3}\)-ions hydrogen-bonded to the area N-III groups.

The event at 1045/1047 cm\(^{-1}\) in the FT-IR (Fig. 9(a)) and FT-Raman (Fig. 9(b)) spectra of the more concentrated samples (c = 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 d-\(\text{U}(2000)_{\text{k}}\) with c ≥ 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 polarizability of the species in question, since this pair of bands has no counterpart in the FT-Raman spectrum (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 KCTF\(_{\text{SO}}\) (42) thus corroborating the above XRD interpretation.

The main conclusion that stems from the spectrophotometric study performed in the present work is that, in accordance with the situation found in analogous long-chain di-ureasil systems\(^{22,23}\) the charge carriers of the conductivity maximum of d-\(\text{U}(2000)_{\text{k}}\)KCTF\(_{\text{SO}}\) are "free" ions or weakly coordinated species.

Electrochemical device performance

To be used in an optical device a polyethylene 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 the colour contrasts.\(^{45}\) Fig. 10 shows the optical reflectance spectra in the wavelength range between 380 and 950 nm for a prototype ECD based on the d-\(\text{U}(2000)_{\text{k}}\)KCTF\(_{\text{SO}}\) 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 95-99% for the bleached state (Fig. 10). The bleaching colouring time was approximately 60 s. The transmission of the coloured state is ~50%, showing a peak value at 430 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 International de l'Éclairage (CIE), using the 2° observer. As shown in the (a,b) 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 diverse cross-linked POE-siloxane (di-unsaturated) network represents a viable and successful alternative in the case of electrolyte systems doped with KSCF$_2$SO$_4$ as the anion. The conductivities obtained here are higher than those reported for the conventional POE-based electrolytes.

Moreover, the encouraging results observed in this study of KSCF$_2$SO$_4$-doped POE-siloxane copolymers confirm the advantages that derive from the use of di-unsaturated monomers 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 sealing 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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References
Scheme 1: Structure of the d-U(2000)xKCF3SO3 di-uramilis.

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)xKCF3SO3 di-uramilis.

Fig. 2: XRD patterns of selected d-U(2000)xKCF3SO3 di-uramilis.

(a) DSC curves of the d-U(2000)xKCF3SO3 di-uramilis, (b) and (c) TGA curves of selected d-U(2000)xKCF3SO3 di-uramilis.

Fig. 4: Arrhenius conductivity plot of the d-U(2000)xKCF3SO3 di-uramilis.
Table 1  Conductivity maxima of polymer electrolyte systems incorporating alkaline, alkaline-earth and transition metal triflate salts

<table>
<thead>
<tr>
<th>System</th>
<th>Ionic conductivity S cm⁻¹</th>
<th>T = 22 °C</th>
<th>T = 100 °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>POP₂₃KCF₃SO₄</td>
<td>9.3 x 10⁻⁴</td>
<td>4.5 x 10⁻⁴</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>d-U(2000)₂₃KCF₃SO₄</td>
<td>1.1 x 10⁻⁴</td>
<td>6.2 x 10⁻⁴</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>d-U(2000)₂₃MgCF₃SO₄</td>
<td>3.8 x 10⁻⁴ (n = 20)</td>
<td>3.1 x 10⁻⁴ (n = 10)</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>d-U(2000)₂₃Mg₂CF₃SO₄</td>
<td>4.0 x 10⁻⁴</td>
<td>6.7 x 10⁻⁴</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>d-U(2000)₂₃Mg₃CF₃SO₄</td>
<td>5.5 x 10⁻⁴ (n = 60)</td>
<td>7.3 x 10⁻⁴ (n = 20)</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5  Room temperature cyclic voltammograms of the d-U(2000)₂₃KCF₃SO₄ di-urea obtained with a gold microelectrode and lithium counter/reference electrode (scan rate 100 mV s⁻¹).

Fig. 6  FT-IR spectra of selected d-U(2000)₂₃KCF₃SO₄ di-urea in the 1800-1600 cm⁻¹ region (v(CO), v(CH₃) and v(SO₃) 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)₂₃KCF₃SO₄ di-urea 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)KCF3SO4 di-annel all at the v(SO4) region. In order to examine exhaustively the contribution of the v(SO4) mode, the FT-Raman spectrum of the pure polyacetol had to be first subtracted from those of the hybrids with n > 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)KCF3SO4 di-annel all in (a) the FT-IR, and (b) FT-Raman v(SO4) region. 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 U(300)KyKCF$_2$SO$_3$ as anolyte in (1) bleached, and (2) coloured states.

Fig. 11 CIE chromaticity diagram (1931) showing the (x,y) colour coordinates of the ECD structure using U(300)KyKCF$_2$SO$_3$ as anolyte in bleached and coloured states.