

# Di-ureasil hybrids doped with LiBF<sub>4</sub>. Part II: Spectroscopic study of the ionic interactions and hydrogen bonding

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## ABSTRACT

In the present work Fourier Transform infrared and Raman spectroscopy were used to characterize the cation/polymer, cation/cross-link, cation/anion and hydrogen bonding interactions in hybrid electrolytes composed of lithium tetrafluoroborate (LiBF<sub>4</sub>) and di-urea cross-linked poly(oxyethylene) (POE)/siloxane hybrid networks (di-ureasils) designated as d-(2000) and d-U(600) and incorporating polyether chains with *ca.* 40.5 and 8.5 oxyethylene repeat units, respectively. Samples with  $\infty > n \geq 2.5$  (where n, composition, is the molar ratio of CH<sub>2</sub>CH<sub>2</sub>O units per Li<sup>+</sup> ion) were analyzed. In both di-ureasil systems over the whole range of salt content examined the Li<sup>+</sup> ions bond to the ether oxygen atoms of amorphous POE chains and to BF<sub>4</sub><sup>-</sup> ions forming ion contact pairs. Spectroscopic evidences and SEM images confirm the presence of a crystalline POE/LiBF<sub>4</sub> complex of unknown stoichiometry at  $n < 20$  and 25, respectively. Ionic association is particularly important in the case of the d-U(600)-based materials, as a result of the presence of strong hydrogen-bonded aggregates that prevent the establishment of Li<sup>+</sup>/urea carbonyl oxygen atom interactions.

**Keywords:** di-ureasils, lithium tetrafluoroborate, FT-IR, FT-Raman

## 1. Introduction

With the advent of the electronic age, we have become increasingly aware that the predictable oil shortage and critical environmental issues demand alternative power sources. We have rapidly entered a new era in which the use of renewable energy sources, portable computing and telecommunication equipments, as well as electric transportation, have become compulsory. Clearly, the emerging new energy economy must rely on a clean, cheap and sustainable energy supply. Battery devices may potentially provide a solution, as they can be employed to store energy from sustainable sources, such as the wind and solar power, in applications ranging from cars to microchips [1]. The present technology does not meet, however, the new power-storage requirements. Electrode and electrolyte systems with superior properties, improved performance and low cost must be developed.

Understandably, research on  $\text{Li}^+$ -based solid polymer electrolytes (SPEs) [2] has been extremely active in the last few years because of the inherent potential application of these materials in light-weight, leakage-free, environmentally friendly and safe solid state electrochemical devices, such as Li-ion batteries [1,3,4]. In this context, the benefits of the organic/inorganic hybrid concept [5], intimately associated with the sol-gel route [6], have been largely explored for the development of organically modified silicate electrolytes (ormolytes) [7-25]. The most attractive advantages associated with this combined synthetic strategy are: (1) Easy processability of the materials into essentially amorphous films of variable flexibility, high transparency and high thermal, mechanical and chemical stability. (2) Possibility of incorporating considerably higher amounts of the guest salt in hybrid matrices than those possible in conventional SPEs, thus avoiding undesirable “salting out” effects.

In this framework our group has devoted considerable efforts to the study of  $\text{Li}^+$ -doped Class II hybrids named di-ureasils [15,18-23]. These ormolytes are di-urea cross-linked poly(oxyethylene) (POE)/siloxane hybrid structures represented by the notation d-U(Y), where d indicates di, U

denotes the urea (-NHC(=O)NH-) group and  $Y = 2000, 900$  and  $600$  represents the average molecular weight of the starting organic precursor (in  $\text{g mol}^{-1}$ ), corresponding to 40.5, 15.5 and 8.5 -CH<sub>2</sub>CH<sub>2</sub>O- repeat units, respectively.

As local segment motion is known to play a key-role in the ionic migration in PEs, the di-ureasil electrolytes which exhibit the highest conductivity are those incorporating the longest POE chains, i.e., the d-U(2000)-based materials [26]. In systems based on the d-U(600) structure, ion transport is reduced, since the segments are too short, causing a restriction in polymer segment mobility. We doped d-U(2000) with lithium triflate (LiCF<sub>3</sub>SO<sub>3</sub>) [15], lithium perchlorate (LiClO<sub>4</sub>) [20] and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) [21]. More recently, in Part I of this series of papers, we incorporated lithium tetrafluoroborate (LiBF<sub>4</sub>) into d-U(2000) and demonstrated that these new materials represent a promising alternative to the LiTFSI- and LiClO<sub>4</sub>-doped POE and POE/siloxane analogues [27]. Curiously, although LiBF<sub>4</sub> is attractive for the production of electrolyte systems for high performance low temperature Li-ion batteries [28-30], the number of studies dealing with PEs doped with LiBF<sub>4</sub> is, however, rather scarce [31-34].

In Part I [27] the thermal, morphological and structural properties of d-U(2000)<sub>n</sub>LiBF<sub>4</sub> samples with  $\infty > n \geq 2.5$  (where  $n$ , composition, is the number of oxyethylene units of the network per Li<sup>+</sup> ion) were investigated. Materials with  $n \geq 20$  exhibit excellent thermal stability (up to 250 °C). While crystalline POE was detected in di-ureasils  $n \geq 15$ , at  $60 \geq n \geq 2.5$  we found evidences of the formation of a crystalline POE/LiBF<sub>4</sub> compound. We also demonstrated that at  $n = 2.5$  the latter crystalline phase coexists with free LiBF<sub>4</sub>. The room temperature conductivity maximum of this ormolyte system is located at  $n = 10$  ( $1.5 \times 10^{-5} \text{ S cm}^{-1}$  at 22 °C). The electrochemical stability of these samples is acceptable for any application in solid state electrochemical device (about 5.5 V *versus* Li/Li<sup>+</sup> at  $n = 15$ ).

In this work the same set of d-U(2000)<sub>n</sub>LiBF<sub>4</sub> hybrid materials has been characterized by Fourier Transform Infrared and Raman (FT-IR and FT-Raman, respectively) spectroscopy with the

primary objective of determining the extent of  $\text{Li}^+/\text{POE}$  and  $\text{Li}^+/\text{BF}_4^-$  interactions. We have also used FT-IR spectroscopy to elucidate, not only the extent and strength of hydrogen bonding interactions in these materials, but also the role of the carbonyl oxygen groups of the urea cross-links in the coordination of the  $\text{Li}^+$  ions. For comparison purposes, we have also examined the  $\text{d-U}(600)_n\text{LiBF}_4$  analogues the conductivities of which have been reported recently elsewhere [35].

The present spectroscopic analysis relies on the fact that the guest anion, i.e.,  $\text{BF}_4^-$ , is a suitable ion probe for the study of ionic association because its vibrational modes are readily identified in the infrared and Raman spectra. Moreover, the attribution of the spectral features of this anion is well documented [36-39].

## 2. Experimental

### 2.1. Preparation of the ormolytes.

See Part I [27] and Ref. 35.

### 2.2. Characterization of the ormolytes.

FT-IR spectra were acquired at room temperature using a Unicam FT-IR spectrophotometer. Solid samples (2 mg) were finely ground, mixed with approximately 175 mg of dry potassium bromide (Merck, spectroscopic grade) and pressed into pellets. Prior to recording the spectra, the disks were vacuum-dried at 80 °C for about 60 h, in order to reduce the levels of adsorbed water and solvent. The spectra were collected in the 4000-500  $\text{cm}^{-1}$  range by averaging 64 scans at a resolution of 4  $\text{cm}^{-1}$ .

FT-Raman spectra were recorded at room temperature with a Bruker RFS 100/S spectrometer equipped with a near-infrared Nd:YAG laser with wavelength excitation (1064 nm at 400 mW). The

spectra were collected over the 3200–300  $\text{cm}^{-1}$  range by averaging 200 scans at a maximum resolution of 4  $\text{cm}^{-1}$ .

To evaluate complex band envelopes and to identify underlying spectral components, the iterative least-squares curve-fitting procedure in the PeakFit software (Jandel Corporation, 2591 Rerner Boulevard, San Rafael, CA 94901, U.S.A.) was used. The best fit of the experimental data was obtained by varying the frequency, bandwidth and intensity of the bands and by using a Gaussian shape. A linear baseline correction with a tolerance of 3% was employed. The standard errors of the curve-fitting procedure were less than 0.005.

To determine the morphology of the as-prepared samples, Scanning Electron Microscopy (SEM) micrographs were obtained using a SEM/ESEM-FEI Quanta 400 equipment operating at a high acceleration voltage (25 kV).

### 3. Results and Discussion

#### 3.1. $\text{Li}^+$ /POE Interactions.

To analyze the interaction of the  $\text{Li}^+$  ions with the POE chains of the host hybrid framework, two spectral regions of the infrared spectra of the  $\text{d-U}(2000)_n\text{LiBF}_4$  samples were inspected: (1) The skeleton COC stretching ( $\nu\text{COC}$ ) region (1200-1000  $\text{cm}^{-1}$ ); (2) The rocking,  $\text{rCH}_2$  region (1000-800  $\text{cm}^{-1}$ ). Both regions are known to be very sensitive to changes occurring in the conformations of the polyether backbone as a result of bonding of the guest cations to the ether oxygen atoms of the solvating chains.

Fig. 1(a) and Fig. 1(c) show the  $\nu\text{COC}$  region of the  $\text{d-U}(2000)_n\text{LiBF}_4$  and  $\text{d-U}(600)_n\text{LiBF}_4$  diureasils, respectively. The results of the curve-fitting performed in the spectra of the two most concentrated samples are reproduced in Fig. 1(b) and Fig. 1(d), respectively. The spectral signature

of the two series of di-ureasils resemble closely. All the materials give rise to a prominent, broad band centered around  $1109\text{ cm}^{-1}$  and a shoulder at about  $1145\text{ cm}^{-1}$  (Fig. 1(a) and Fig. 1(c)). These events are ascribed to the  $\nu\text{COC}$  vibration mode and to the coupled vibration of the  $\nu\text{COC}$  and  $\text{rCH}_2$  modes, respectively, and are characteristic of non-coordinated, disordered POE chains [40,41].

The feature located at  $1083\text{ cm}^{-1}$  in the FT-IR spectra of all the doped samples of both series of hybrids (Fig. 1(a) and Fig. 1(c)), the intensity of which is enhanced with the guest salt content, reveals that the  $\text{Li}^+$  ions are complexed by the oxygen atoms of amorphous POE chains over the entire range of salt content studied [16,22,42]. The band visible at  $1123\text{ cm}^{-1}$  and the event discerned at  $1096\text{ cm}^{-1}$  in the FT-IR spectra of the  $\text{d-U}(2000)_n\text{LiBF}_4$  (Fig. 1(b)) and  $\text{d-U}(600)_n\text{LiBF}_4$  (Fig. 1(d)) samples with  $n = 5$  and  $2.5$  are indicative of the formation of a crystalline POE/ $\text{LiBF}_4$  complex of unknown stoichiometry. These results confirm that in the salt-rich samples non-coordinated and coordinated amorphous POE chains coexist with the crystalline POE/ $\text{LiBF}_4$  compound. However, the formation of the complex is definitely initiated at lower salt content. The beginning of such process is difficult to establish exactly, as it depends critically on the technique used. For instance, in the case of the  $\text{d-U}(2000)$ -based di-ureasils, the POE/ $\text{LiBF}_4$  compound was identified by DSC at  $n = 5$  and by XRD at  $60 \geq n \geq 8$  [27]. In the FT-IR spectra of Fig. 1(a) the first signs of the emergence of such compound are discerned at  $n = 20$ . Similarly, while the XRD patterns of the  $\text{d-U}(600)_n\text{LiBF}_4$  hybrids revealed the presence of the same crystalline phase for  $n \leq 10$  [27], the FT-IR spectrum of the sample with  $n = 35$  (Fig. 1(c)) suggests that the formation of the crystalline complex occurs in the medium-low salt content range.

In the  $\text{rCH}_2$  region the FT-IR spectra of the  $\text{LiBF}_4$ -based hybrids with  $n \geq 20$  (Fig. 2(a)) and  $n \geq 25$  (Fig. 2(b)) closely resemble those of  $\text{d-U}(2000)$  (Fig. 2(a)) and  $\text{d-U}(600)$  (Fig. 2(b)), respectively. In these concentration ranges the dominant features produced are two broad, medium intensity bands characteristic of amorphous poly(ethylene glycol) (PEG) chains [40,41]: a band located at  $950\text{ cm}^{-1}$ , attributed to the coupled vibration of the  $\nu\text{CC}$  and  $\text{rCH}_2$  modes, and a less intense and ill-defined,

event at  $847\text{ cm}^{-1}$ , due to the coupled vibration of the  $\nu\text{COC}$  and  $\text{rCH}_2$  modes. Upon incorporation of more salt ( $n < 20$  for the d-U(2000)-based samples and  $n < 25$  for the d-U(600)-based samples) the contour of the  $\nu\text{CC}/\text{rCH}_2$  ( $980\text{-}900\text{ cm}^{-1}$ ) and  $\nu\text{COC}/\text{rCH}_2$  ( $900\text{-}780\text{ cm}^{-1}$ ) envelopes is changed, the effects being clearly more marked in the family of di-ureasils including shorter POE chains (Fig. 2(b)). The band at  $847$  is downshifted to  $843\text{ cm}^{-1}$  (Fig. 2(a) and Fig. 2(b)). In addition, in the spectra of the d-U(2000)<sub>n</sub>LiBF<sub>4</sub> hybrids a shoulder develops at  $937\text{ cm}^{-1}$  (Fig. 2(a)) and in those of the d-U(600)<sub>n</sub>LiBF<sub>4</sub> materials a distinct band grows at  $881\text{ cm}^{-1}$  (Fig. 2(b)). The emergence of the features at  $937$  and  $843\text{ cm}^{-1}$ , characteristic of crystalline, non-coordinated hepta(ethyleneglycol) dimethyl ether (HEGDME) and PEG [42], respectively, may be interpreted as an indication that in the d-U(2000)<sub>n</sub>LiBF<sub>4</sub> ormolytes with  $n = 5$  and  $2.5$  and the d-U(600)<sub>n</sub>LiBF<sub>4</sub> hybrids with  $n = 10, 5$  and  $2.5$  a proportion of the POE segments adopt a helical-like structure and therefore *gauche* O-C-C-O conformations to bond to the Li<sup>+</sup> ions and subsequently give rise to the formation of the crystalline POE/LiBF<sub>4</sub> complex. The band produced at  $881\text{ cm}^{-1}$  by the d-U(600)-based di-ureasils with  $n \leq 10$  represents another manifestation of the presence of this compound [16].

Seeking further evidences of the occurrence of POE/LiBF<sub>4</sub>, we recorded the FT-Raman spectra of the same materials in the region characteristic of the “oxygen breathing mode” [43]. At  $n \geq 20$  the FT-Raman spectra of the non-doped and doped d-U(2000)<sub>n</sub>LiBF<sub>4</sub> di-ureasils are very similar, being dominated by a feature at  $843\text{ cm}^{-1}$  (Fig. 3(a)). At  $n = 5$  and  $2.5$  the band profile changes drastically and a strong feature emerges near  $864\text{ cm}^{-1}$  (Fig. 3(a)). Accordingly, the FT-Raman spectra of the d-U(600)<sub>n</sub>LiBF<sub>4</sub> di-ureasils with  $n \geq 25$ , which are practically identical, exhibit a prominent feature centered at  $848\text{ cm}^{-1}$  (Fig. 3(b)). At higher concentration, the strongest event is a band at  $860\text{ cm}^{-1}$  (Fig. 3(b)). Three events located at *ca.*  $946, 936$  and  $930\text{ cm}^{-1}$  are also evident in the FT-Raman spectrum of the d-U(600)<sub>2.5</sub>LiBF<sub>4</sub> xerogel (Fig. 3(b)). The  $864/860\text{ cm}^{-1}$  band (Fig. 3(a)/Fig.3(b)), which grows with salt content, is associated with a symmetric stretching vibration mode ( $\nu\text{M-O}_m$ ) that accompanies wrapping of the POE chains around the Li<sup>+</sup> ion during complexation and is

consequently indicative of the presence of *gauche* conformations in the O-C-C-O- sequences [36,44,45]. We note in parallel a reduction in the intensity of a band situated near 807/811  $\text{cm}^{-1}$  as the salt concentration is increased (Fig. 3(a)/Fig.3(b)). This feature, evident in the FT-Raman spectra of all the xerogels, is characteristic of the occurrence of *trans* conformations in the -O-C-C-O- sequences of the POE chains [46,47]. The progressive increase of the relative intensity between the 864/860  $\text{cm}^{-1}$  and 807/811  $\text{cm}^{-1}$  bands as more  $\text{LiBF}_4$  is added to d-U(2000)/d-U(600) is in perfect agreement with the increase of the proportion of *gauche* conformers and the concomitant reduction of the proportion of *trans* conformers.

The determination of the composition at which the cation/ether oxygen coordination is initiated in PEs is always a matter of intense debate. In the present case, while the first signs have been detected in the  $\nu\text{COC}$  region already in the most dilute material ( $n = 200$ ) in both families of di-ureasils, in the  $\text{rCH}_2$  region several spectroscopic evidences point out that such interaction begins at  $n < 20$  and  $n < 25$  for the d-U(2000)- and d-U(600)-based materials, respectively. We note that the conclusions retrieved from the latter spectral region correlate well with the trend of the composition dependence of the glass transition temperature ( $T_g$ ) reported for the two families of hybrids [27,35]. This induces us to suggest that in the  $200 \geq n \geq 20/25$  composition range the number of  $\text{Li}^+$ /POE bonds is very likely too low to influence the contour band of the conformation sensitive  $\text{rCH}_2$  bands and also the  $T_g$  of the samples. Clearly the crystalline phase is readily identified in both spectral regions examined here.

Interestingly, the data discussed in this sections strongly suggest that the beginning of  $\text{Li}^+$ /POE interaction in the two di-ureasils families studied is apparently independent of the length of the POE chains.

**$\text{Li}^+/\text{BF}_4^-$  Interactions.** The “free” tetrahedral  $\text{BF}_4^-$  ion, with point group  $T_d$ , has nine Raman active vibration normal modes: the non-degenerate mode  $\nu_1(A_1)$ ; the doubly degenerate mode  $\nu_2(E)$ ; the triply degenerate modes  $\nu_3(T_2)$  and  $\nu_4(T_2)$ . Only  $\nu_3(T_2)$  and  $\nu_4(T_2)$  are infrared active. Cation



coordination lowers the local symmetry around  $\text{BF}_4^-$ . This effect is evident in the spectra through band splitting of degenerate vibrations; frequency shifts of non-degenerate vibrations and activation of the infrared-forbidden  $\nu_1$  and  $\nu_2$  modes.

The presence of the infrared inactive  $\nu_1$  mode at  $770/771\text{ cm}^{-1}$  in the FT-IR spectra of the  $\text{LiBF}_4^-$  doped d-U(2000)- and d-U(600)-based di-ureasils (Fig. 4) confirms the existence of ion pairs over the whole range of salt composition investigated [26]. In the case of the d-U(600)<sub>n</sub> $\text{LiBF}_4$  system, the  $\nu_1$  band is considerably more intense, a result that gives support to the explanation that in these materials a higher amount of such coordinated species exist. The events at  $574/575$ ,  $534$  and  $522/520\text{ cm}^{-1}$  (Fig. 4) are tentatively attributed to the lifting of the degeneracy of the  $\nu_4\text{BF}_4$  mode resulting from the formation of ion pairs in a presumably *bidentate* coordination [26]. This type of bonding configuration would imply the association of the  $\text{Li}^+$  ion with two of the  $\text{BF}_4^-$  fluorine atoms.

These spectroscopic data support the suggestion that in the di-ureasil samples examined there is a clear tendency for ionic association. This effect is particularly important in the case of the d-U(600)-based materials. Unfortunately, the complexity of the band envelopes does not allow establishing a direct correspondence between the concentration of “free” ions and the ionic conductivity.

***Li<sup>+</sup>/urea cross-link interactions.*** In addition to interacting with the oxygen atoms of the POE chains and with the  $\text{BF}_4^-$  ions, as demonstrated in the previous sections, the  $\text{Li}^+$  ions incorporated into the two di-ureasil frameworks considered have the possibility of interacting with the urea linkages. They may bond to the oxygen atoms of “free” (non-bonded) C=O groups and/or to C=O groups belonging to hydrogen-bonded aggregates. Obviously, in the latter case the alkali metal ions need to disrupt hydrogen bonds.

The two di-ureasil networks used in the present work differ significantly from the standpoint of hydrogen bonding. In d-U(600), which contains short polymer chains and a very high proportion of urea cross-links, ordered and strong urea/urea aggregates forming planar bifurcated hydrogen bonds largely dominate, whereas the fraction of POE/urea associations is less important and that of “free”

urea groups is almost negligible. The reverse situation occurs in d-U(2000). In this matrix, composed of long POE segments and a low concentration of urea groups, most of the urea cross-links are non-bonded or forming POE/urea aggregates.

Rich information regarding, not only the extent and magnitude of hydrogen bonding, but also the formation of  $\text{Li}^+$ /urea interactions, may be retrieved from the analysis of “amide I region (1800-1600  $\text{cm}^{-1}$  interval) in the FT-IR spectra. The “amide I” band of the di-ureasils corresponds to the amide I [48] band of polyamides [49]. The amide I mode (or simply carbonyl stretching mode) is a very complex vibration that receives a major contribution from the C=O stretching vibration [49] and is sensitive to the specificity and magnitude of hydrogen bonding. In general the amide I band is manifested as a broad envelope that may be resolved into several distinct components which correspond to different C=O environments often called aggregates. Because the absorption coefficients of the C=O groups belonging to different aggregates may be different, concentration variations of each aggregate can only be deduced from the variations of the corresponding component [49,50].

The “amide I” band of d-U(2000)/d-U(600) was resolved into components at 1751, 1724/1714, 1675/1682, 1657/1654 and 1643/1636  $\text{cm}^{-1}$  (Fig. 5(a)/Fig. 5(c)) [16,51,52]. The band at 1751  $\text{cm}^{-1}$  is due to the absorption of urea groups in which the N-H or C=O groups do not participate in any hydrogen bonding interactions [16,51,52]. The bands at 1724/1714, 1675/1682 and 1657/1654  $\text{cm}^{-1}$  are ascribed to C=O groups of disordered hydrogen-bonded POE/urea aggregates of increasing strength [16,51,52]. The 1643/1636  $\text{cm}^{-1}$  feature is assigned to C=O groups included in significantly more ordered hydrogen-bonded urea/urea aggregates [16,51,52].

Fig. 5(a) and Fig. 5(b) demonstrate that the addition of  $\text{Li}^+$  ions to d-U(2000) alters drastically the “amide I” envelope, an indication that the cations interact markedly with the urea C=O groups over the whole range of salt concentration studied. Globally, the increase of  $\text{LiBF}_4$  content has two major consequences: (1) At  $n = 5$  the 1752 and 1721  $\text{cm}^{-1}$  features vanish, meaning that all the C=O

groups become saturated and that the most disordered POE/urea aggregates are completely destroyed, respectively. (2) A new event emerges at  $1704\text{ cm}^{-1}$  immediately upon doping, suggesting the formation of new POE/urea aggregates. In contrast, the incorporation of the guest salt into the d-U(600) matrix has minor consequences on the proportion of POE/urea and urea/urea hydrogen-bonded arrays (Fig. 5(c) and Fig. 5(d)).

The variation of the integral area of the “amide I” components with the amount of salt in the d-U(2000)<sub>n</sub>LiBF<sub>4</sub> (Fig.6(a) not shown) and d-U(600)<sub>n</sub>LiBF<sub>4</sub> (Fig. 6(b) not shown) systems corroborates both conclusions. The complex trend observed in the case of the former family of di-ureasils shows that all the components are subject to changes upon salt addition. In the d-U(600)-based materials the only important effects worth noting occur near  $n = 15$  and involve a drastic enhancement of the proportion of urea/urea aggregates at the expense of the breakdown of urea/POE aggregates (not shown Fig. 6(b)). The destruction of the latter hydrogen-bonded associations is most likely a consequence of the fact that around that composition the POE chains are being massively required to complex the Li<sup>+</sup> ions and presumably form the crystalline POE/LiBF<sub>4</sub>.

These findings may be interpreted as proofs that in the d-U(600)-based medium, in which strong urea/urea aggregates dominate, bonding to the urea carbonyl oxygen atoms is inhibited, thus promoting bonding of the Li<sup>+</sup> ions to the oxygen atoms of the POE chains and in particular to the BF<sub>4</sub><sup>-</sup> ions. In the d-U(2000) matrix, which provides a high proportion of “free” carbonyl groups and contains a high fraction of disordered (and thus easily disrupted) POE/urea aggregates, the coordination of the cations to the carbonyl oxygen atoms is favored. In the latter system, bonding to the POE chains and ionic association occur simultaneously, although the latter process takes place in a lesser extent. It is of interest to mention that the behavior of the d-U(600) matrix toward LiBF<sub>4</sub> differs from that observed in the presence of Eu(ClO<sub>4</sub>)<sub>3</sub>, since in the latter case at  $n < 62$  the disruption of the hydrogen-bonded urea-urea structures becomes possible, allowing the carbonyl oxygen atoms of the urea groups to participate actively in the coordination of the Eu<sup>3+</sup> ions [52].

The SEM images of Fig. 6 7(a) and Fig. 7 8(a) show that the d-U(2000) and d-U(600) host hybrid matrices display a non-porous, homogenous texture. The d-U(2000)-based sample with  $n=40$  gives exhibits distinct micrometric aggregates of crystalline POE material dispersed within the hybrid framework (Fig. 67(b)), corroborating the XRD data [27]. The SEM image of the  $n = 2.5$  material reveals the presence of a highly ordered phase (Fig. 67(c)) that unequivocally corresponds to the crystalline POE/LiBF<sub>4</sub> complex identified here by FT-IR and previously reported on the basis of XRD and DSC data [27]. The changes to which the morphology of the d-U(600)<sub>n</sub>LiBF<sub>4</sub> samples are subject at increasing salt content may be deduced from Fig.7 8. While the materials with  $n = 60$  (Fig. 78(b)) and 35 (Fig. 78(c)) display a granular-like texture, the xerogel with  $n = 10$  (Fig. 78(d)) produces aggregates of variable shape composed of cubic-like micro-objects, presumably associated with the presence of the crystalline POE/LiBF<sub>4</sub> complex. At  $n=5$  the latter objects coexist with plates (Fig. 78(e)). The most concentrated sample exhibits cubic-like micro-objects regularly distributed throughout the material (Fig. 78(f)).

#### 4. Conclusion

In the present work we have shown by means of Fourier Transform infrared and Raman spectroscopy that the coordination processes in two di-ureasil electrolyte hybrid media doped with LiBF<sub>4</sub> depend critically on the length of the POE chains of the host hybrid network and thus on the concentration of urea cross-linkages. Li<sup>+</sup> bonding to amorphous POE chains and Li<sup>+</sup>/BF<sub>4</sub><sup>-</sup> ion contact pairs have been detected over the whole wide range of salt concentration examined. In the short chain hybrid system ionic association is, however, more marked. In both types of host matrices a crystalline POE/LiBF<sub>4</sub> complex is formed at high salt content. The addition of the guest salt has dramatic implications in the hydrogen-bonded array of the long chain di-ureasil framework and Li<sup>+</sup> bonding to the C=O groups occurs extensively. In contrast, the hydrogen bonding interactions in the short chain analogues remain practically unaffected by salt addition.

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