

**PREPARATION OF HYBRID ORGANIC-INORGANIC MATERIALS BASED ON  
A DI-UREASIL MATRIX DOPED WITH LITHIUM  
BIS(TRIFLUOROMETHANESULFONYL)IMIDE**

P. C. Barbosa, L. C. Rodrigues, M. M. Silva\* and M. J. Smith

CQ-FCT, Universidade do Minho, Gualtar 4710-057 Braga, Portugal

**Abstract**

In this presentation we describe the preparation of solvent-free solid polymer electrolytes (SPEs) by the sol-gel route with the incorporation of controlled quantities of lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) into the host matrix. The host framework of these xerogels, designated as di-ureasils and represented by d-U(900), contains oxyethylene oligomers with about 15 repeat units bonded at each end to a siliceous backbone through urea bridging links. Electrolytes were characterized by ionic conductivity measurements, cyclic voltammetry at a gold microelectrode and thermal analysis. The results obtained reveal that these hybrid materials are completely amorphous and exhibit appropriate electrochemical characteristics for a variety of applications.

**Keywords:** di-ureasils, sol-gel process, polymer electrolytes, complex impedance spectroscopy

---

\* Corresponding author. Tel: +351 253604370, +351 253604386; Fax: +351 253604382.  
E-mail address: nini@quimica.uminho.pt

## **1. Introduction**

The technological advances in mobile telephones, laptops and both hybrid and plug-in electric vehicles have been closely followed by the development of high-performance portable energy sources. Lithium-ion batteries are particularly well-adapted as energy sources for a wide variety of devices, offering reliability and appropriate performance levels of critical operating parameters [1-4].

A sub-class of SPEs, designated as ormolytes (organically modified electrolytes), has attracted particular attention. The sol-gel synthetic strategy offers an extremely flexible route to hybrid organic-inorganic materials from reactive, high-purity molecular precursors under mild reaction conditions and provides a method by which the properties of target molecules can be tailored by fine-tuning the synthetic procedures [5, 6]. The resulting hybrid materials may find applications in a variety of devices including advanced batteries, sensors, electrochromic displays, smart labels and windows. Hybrid network structures based on di-ureasils have already been shown to be well-suited as multi-functional components (electrolyte, separator, adhesive and sealant) in electrochromic devices and their good mechanical, chemical, thermal and electrochemical properties, may also make them an appropriate choice for application in advanced batteries.

The encouraging ionic conductivity reported for previously characterized polymer electrolyte systems incorporating  $\text{Li}^+$  ions prompted us to study a series of LiTFSI-doped poly(oxyethylene) (PEO)/siloxane xerogels with potential application as electrolytes in the manufacture of advanced batteries.

## **2. Experimental Details**

### *2.1. Materials*

Lithium bis(trifluoromethanesulfonyl)imide was dried under vacuum at 190°C for 7 days and then stored in a high integrity, dry argon-filled glovebox. This procedure was applied to establish the initial anhydrous state of the lithium salt. The O,O'-bis(2-aminopropyl) polyethylene glycol (commercially available as Jeffamine ED-900®, Fluka, average molecular weight 900 g mol<sup>-1</sup>) was dried under vacuum at 25°C for several days prior to use. The bridging agent, 3-isocyanatepropyltriethoxysilane (ICPTES, Aldrich 95%), was used as received. Ethanol (CH<sub>3</sub>CH<sub>2</sub>OH, Merck, 99.8%) and tetrahydrofuran (THF, Merck, 99.9%) were dried over molecular sieves. High purity distilled water was used in all experiments.

## 2.2. Sample preparation

The preparation of Li<sup>+</sup>-doped di-ureasils has been described in detail elsewhere [7, 8]. The procedure used for d-U(900)<sub>n</sub>LiTFSI involved grafting a diamine containing approximately 15 oxyethylene repeat units onto the ICPTES precursor, to yield the di-urea bridged hybrid precursor. This material was subsequently hydrolyzed and condensed in the sol-gel stage of the synthesis to induce the growth of the siloxane framework (Scheme 1).

*Step 1 - Synthesis of the di-ureasil precursor, d-UPTES(900):* 2.0 g of Jeffamine ED-900® was dissolved in 10 ml of THF with stirring. A volume of 1.097 mL of ICPTES was added to this solution in a fume cupboard (molar proportion of 1 Jeffamine ED-900®: 2 ICPTES). The flask was then sealed and the solution stirred for about 12 h at approximately 40°C. A urea-bridged organic-inorganic hybrid intermediate, designated as di-ureapropyltriethoxysilane (d-UPTES(900)), was obtained under these conditions. The grafting process was followed by infrared monitoring.

*Step 2 - Synthesis of the di-ureasil xerogels, d-U(900)<sub>n</sub>LiTFSI:* A volume of 1.038 mL of ethanol, a known mass of anhydrous LiTFSI and 0.120 mL of water were added to the d-UPTES(900) solution prepared in the previous step (molar proportion of 1 ICPTES: 4 ethanol: 1.5 H<sub>2</sub>O). The mixture was stirred, at room temperature, in a sealed flask for approximately 30 min and then decanted into a Teflon® mould, covered with a perforated membrane of Parafilm® and stored in a fume cupboard for 24 h. The mould and contents were then transferred to an oven at 50°C and the sample was aged for a period of 3 weeks. A final aging treatment of 1 week at 80°C completed the preparative process.

### **2.3. Measurements**

#### *2.3.1. Thermal analysis*

Electrolyte sample sections were removed from dry films and subjected to thermal analysis under a flowing argon atmosphere between -60 and 300°C and at a heating rate of 5°C.min<sup>-1</sup> using a Mettler DSC 821e. All samples were presented for analysis in 40 µL aluminium cans with perforated lids to permit the release and removal of decomposition products.

Samples for thermogravimetric studies were prepared in an identical manner, transferred to open platinum crucibles and analyzed using a Rheometric Scientific TG 1000 thermobalance operating under a flowing argon atmosphere. A heating rate of 10°C.min<sup>-1</sup> was used to analyze all the di-ureasil samples.

#### *2.3.2. Impedance spectroscopy*

Total ionic conductivities of electrolyte samples were determined using a constant volume support [9] equipped with gold blocking electrodes and located within a Buchi TO

50 oven. The sample temperature was evaluated by means of a type K thermocouple placed close to the electrolyte film and impedance measurements were carried out at frequencies between 96kHz and 500mHz with a Solartron 1250 FRA and 1286 ECI, over a temperature range of 20 to 90°C. Measurements of conductivity were effected during heating cycles. The reproducibility of recorded conductivities was confirmed by comparing the results obtained for a sample subjected to two heating-cooling-heating cycles. This procedure demonstrated the correct operation of the support and the mechanical stability of the samples.

### *2.3.3. Electrochemical stability*

Evaluation of the electrochemical stability window of electrolyte compositions was carried out under an argon atmosphere using an asymmetrical two-electrode cell configuration. The preparation of a 25 $\mu$ m diameter gold microelectrode surface, by polishing with a moist cloth and 0.05  $\mu$ m alumina powder (Buehler), was completed outside the drybox. The microelectrode was then washed with THF (Aldrich, 99.9% inhibitor-free), dried with a hot-air blower and passed through a purged transfer port into the drybox. The cell was assembled by locating a freshly-cleaned lithium disk counter electrode (cut from Aldrich 20mm wide ribbon 99.9%, 19mm diameter, 0.75mm thick) onto a stainless steel current collector and centering a disk of electrolyte on the clean electrode surface. The microelectrode was then positioned on the electrolyte surface and supported firmly by means of a clamp. An Autolab PGSTAT-12 (Eco Chemie) was used to record voltammograms at a scan rate of 100mV/s. Measurements were performed over a programmed voltage range at room temperature, within a Faraday cage.

### 3. Results and discussion

#### 3.1. Thermal behavior of electrolytes

The results of thermal analysis of the d-U(900)<sub>n</sub>LiTFSI electrolytes are illustrated in Figure 1. No endotherms associated with either the fusion of oxyethylene chain segments or the evaporation of water or ethanol were observed, which allows us to conclude that the samples with  $n$  ranging from 200 to 5 are completely amorphous. At high salt concentration ( $n = 0.5$ ) an endothermic peak is observed at approximately 150°C. Given the absence of weight loss over the relevant temperature range this sharp, symmetrical, endothermic peak has been attributed to the fusion of a salt–polymer complex. Other examples of complex fusion over a similar temperature range have already been reported for di-ureasil systems based on lithium salts [10].

The onset of thermal decomposition was estimated by extrapolation from thermogravimetric analysis curves (Figure 2). The lowest decomposition temperature observed with the d-U(900)<sub>n</sub>LiTFSI system was registered for the  $n = 40$  composition (358°C), which indicates that this di-ureasil system is more stable than corresponding d-U(900)<sub>n</sub>LiClO<sub>4</sub> electrolytes. It is evident that the presence of the guest salt destabilizes the polymer matrix, however there is apparently no direct relationship between the onset of weight loss and the amount of salt present in the electrolyte. This situation is similar to that observed with electrolytes of other di-ureasil systems [11, 12].

The glass transition temperature,  $T_g$ , can be defined as the temperature at which the polymer chains in the amorphous phase begin segmental motion [13]. Figure 3 illustrates the variation of  $T_g$  for selected compositions of the d-U(900)<sub>n</sub>LiTFSI electrolytes. The incorporation of guest salt leads to an increase in  $T_g$ , which means that the electrolyte sample becomes less flexible. Compositions with the highest salt content ( $n = 0.5$  and 1)

presented poor mechanical properties, an aspect that in practical devices limits the usefulness of the electrolyte.

### 3.2. Ionic conductivity of electrolytes

Figure 4 shows the variation of d-U(900)<sub>n</sub>LiTFSI polymer electrolyte conductivity as a function of temperature and confirms that the most conducting composition of this system is d-U(900)<sub>15</sub>LiTFSI which reaches  $7.6 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$  at 95°C. At room temperature the composition with the highest conductivity is d-U(900)<sub>25</sub>LiTFSI ( $2.9 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$ ). It is also clear that the materials characterized in this study show a non-linear variation of log conductivity with  $1/T$  in the range between 25 and 100°C. This behavior is characteristic of amorphous polymer electrolytes. The conductivity isotherms of this electrolyte system are illustrated in Figure 5 and confirm that ionic transport in this hybrid electrolyte system is almost independent of the salt content over a wide range of composition. The broad conductivity maxima is located between  $n = 15$  and 25. Further increase in salt content beyond about  $n = 15$  results in a decrease in total ionic conductivity. This observation is consistent with a decrease in the flexibility of the host polymer chain segments, confirmed by an increase in  $T_g$  of the electrolyte matrix. As the mechanism of ion transport in amorphous polymer electrolytes is dependent on the motion of polymer chain segments, the ionic conductivity is expected to decrease with an increase in  $T_g$  (Figure 6). The observed increase in  $T_g$  at lower values of  $n$  can be explained by the increase in number of bridging interactions that take place between adjacent polymer chains and guest salt species, generally designated as “ionic crosslinking”. As the guest species concentration increases in the polymer electrolyte, the formation of associated ionic species (e.g., contact ion pairs, triplets or higher ion aggregates) also increases and as these aggregates may be expected to

show lower mobility than dissociated ions, this effect also contributes to the observed reduction in the electrolyte conductivity.

Figure 7 compares the ionic conductivity of two di-ureasil systems with the same host matrix [11]. While at temperatures higher than 60°C d-U(900)<sub>n</sub>LiClO<sub>4</sub> ormolytes are more conducting than comparable d-U(900)<sub>n</sub>LiTFSI materials, at lower temperatures the difference is negligible and LiTFSI is a better choice for safety reasons.

### *3.3. Electrochemical stability*

Figure 8 shows a typical voltammogram of the xerogel material with composition n = 20. The electrochemical stability range of the lithium-doped di-ureasils was determined by microelectrode cyclic voltammetry over the potential range between -2.0V and 6.5V. The onset of the current at 5.0 V shows an acceptable stability window of the d-U(900)<sub>n</sub>LiTFSI system and therefore confirms applicability in various electrochemical devices.

## **4. Conclusions**

The results obtained in this study of a novel lithium ion conducting polymer confirm that the electrolyte system described has moderate levels of conductivity and good thermal and electrochemical stability. In practical devices, such as primary or secondary lithium cells, high ionic conductivity and electrochemical stability are of paramount importance, however dimensional stability is also a critical performance parameter. For application in commercial devices the dimensional stability of electrolyte should be comparable to that of porous polymer membranes currently used as battery separators. The preparation of a conventional polymer electrolyte (defined in this context as an ion-conducting matrix

composed of one or more polymers and an ionic guest salt [14]) that satisfies all the relevant criteria has proved to be an elusive goal. In view of the influence that the components of the polymer chain have on the mechanical properties, and on the ionic transport in the electrolyte, it seems likely that the conductivity maximum in polymer electrolyte systems may be limited to about  $10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}$  at room temperature. In spite of the considerable effort that has been dedicated to the search for high-performance electrolytes, few SPE electrolytes have exceeded this limit.

In different applications, such as optical displays, smart windows or time-lapse labels, other aspects of electrolyte performance may assume importance. Electrolytes with appropriate mechanical characteristics, that function as a combined separator/adhesive/sealant component in a thin, multi-layer device may also be of interest. In exploratory studies the electrolyte system described performed satisfactorily as a multi-functional component in a prototype optical device with encouraging characteristics. In this case optical transparency, an aspect of no significance in battery applications, was also favorable. In view of the advantage that the sol-gel method offers in optimization of the composition and properties of hybrid materials, further attention is being devoted to improving various properties of the polymolytes presented.

### **Acknowledgements**

The authors are pleased to acknowledge the support provided by University of Minho and the *Fundação para a Ciência e Tecnologia* (contracts POCI/QUI/59856/2004, POCTI/3/686, SFRH/BD/22707/2005) for staff and laboratory facilities.

## References

- [1] J. R. MacCallum, C. A. Vincent, *Polymer Electrolyte Reviews*, vol. 1 and 2, Elsevier, London, 1987 and 1989.
- [2] R. G. Linford (Ed.), *Electrochemical Science and Technology of Polymers*, vol. 1 and 2, Elsevier, Amsterdam, 1987 and 1991.
- [3] F. M. Gray (Ed.), *Solid Polymer Electrolytes: Fundamentals and Technological Applications*, VCH Publishers, New York, 1991.
- [4] B. Scrosati, *Applications of Electroactive Polymers*, Chapman and Hall, London, 1993.
- [5] C. J. Brinker, G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, CA, 1990.
- [6] P. Gomez-Romero, C. Sanchez (Eds.), *Functional Hybrids Materials*, Wiley Interscience, New York, 2003.
- [7] S.M. Gomes Correia, V. de Zea Bermudez, M.M. Silva, S. Barros, R.A. Sá Ferreira, L.D. Carlos, A.P. Passos de Almeida, M.J. Smith, *Electrochimica Acta* 47 (2002) 2421.
- [8] S.C. Nunes, V. de Zea Bermudez, D. Ostrovskii, L.D. Carlos, *Journal of Molecular Structure* 702 (2004) 39.
- [9] C.J.R. Silva, M. J. Smith, *Electrochimica Acta* 40 (1995) 2389.
- [10] S. C. Nunes, V. de Zea Bermudez, D. Ostrovskii, M. M. Silva, S. Barros, M. J. Smith, L. D. Carlos, J. Rocha, E. Morales, *Journal of The Electrochemical Society*, 152 (2005) A429.
- [11] P.C. Barbosa, M.M. Silva, M.J. Smith, A. Gonçalves, E. Fortunato, *Electrochimica Acta* 52 (2007) 2938.

- [12] M.M. Silva, S.C. Nunes, P.C. Barbosa, A. Evans, V. de Zea Bermudez, M.J. Smith, D. Ostrovskii, *Electrochim. Acta* 52 (2006) 1542.
- [13] F.M. Gray, in *Polymer Electrolytes*, RSC Materials Monographs, Royal Society of Chemistry, London, (1997).
- [14] K. M. Abraham, *Highly conductive polymer electrolytes in: Applications of Electroactive Polymers*, B. Scrosati (ed.), Chapman and Hall, London (1993).

### **Figure captions**

Figure 1. DSC thermograms of selected d-U(900)<sub>n</sub>LiTFSI di-ureasils.

Figure 2. TGA curves of selected d-U(900)<sub>n</sub>LiTFSI di-ureasils. Inset shows extrapolated onset of degradation temperatures.

Figure 3. Extrapolated onset of glass transition temperatures of d-U(900)<sub>n</sub>LiTFSI ormolytes.

Figure 4 a) and b). Variation of conductivity of selected d-U(900)<sub>n</sub>LiTFSI di-ureasils with temperature.

Figure 5. Isothermal variation of ionic conductivity of d-U(900)<sub>n</sub>LiTFSI di-ureasils.

Figure 6. Comparison of variation of  $T_g$  and ionic conductivity of the electrolyte system (30°C) as a function of composition.

Figure 7. Comparison of ionic conductivity of d-U(900)<sub>n</sub>LiTFSI and d-U(900)<sub>n</sub>LiClO<sub>4</sub> di-ureasils.

Figure 8. Voltammogram of d-U(900)<sub>20</sub>LiTFSI electrolyte at a 25 μm diameter gold microelectrode versus Li/Li+. Initial sweep direction is anodic and sweep rate is 100 mVs<sup>-1</sup>.

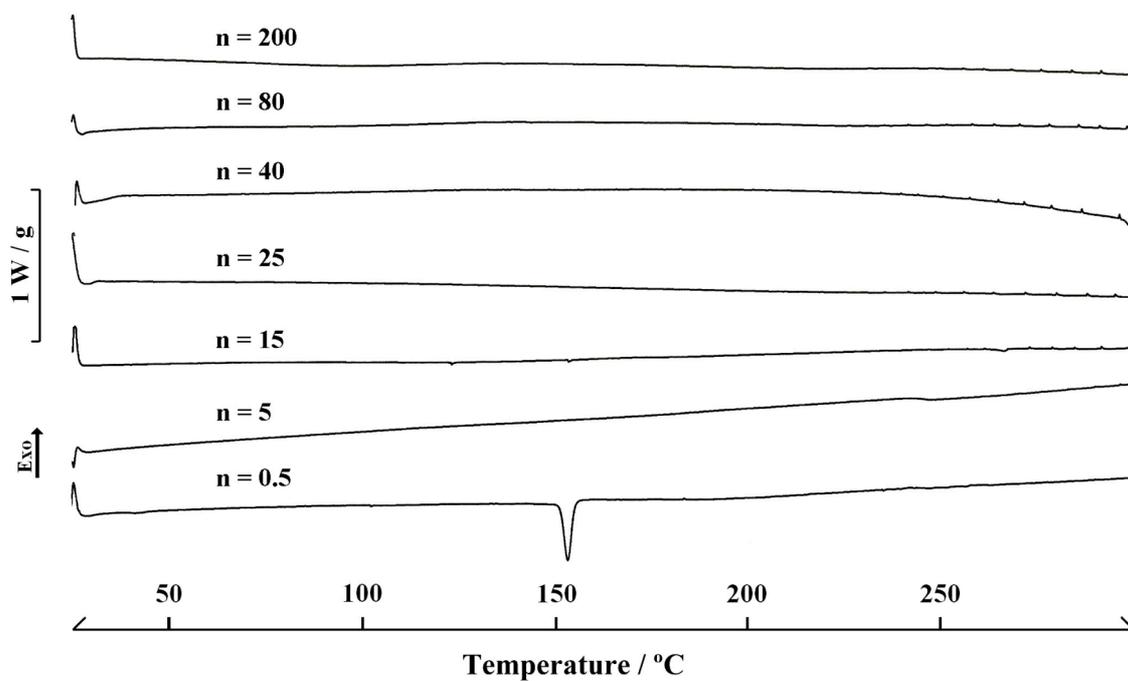


Figure 1

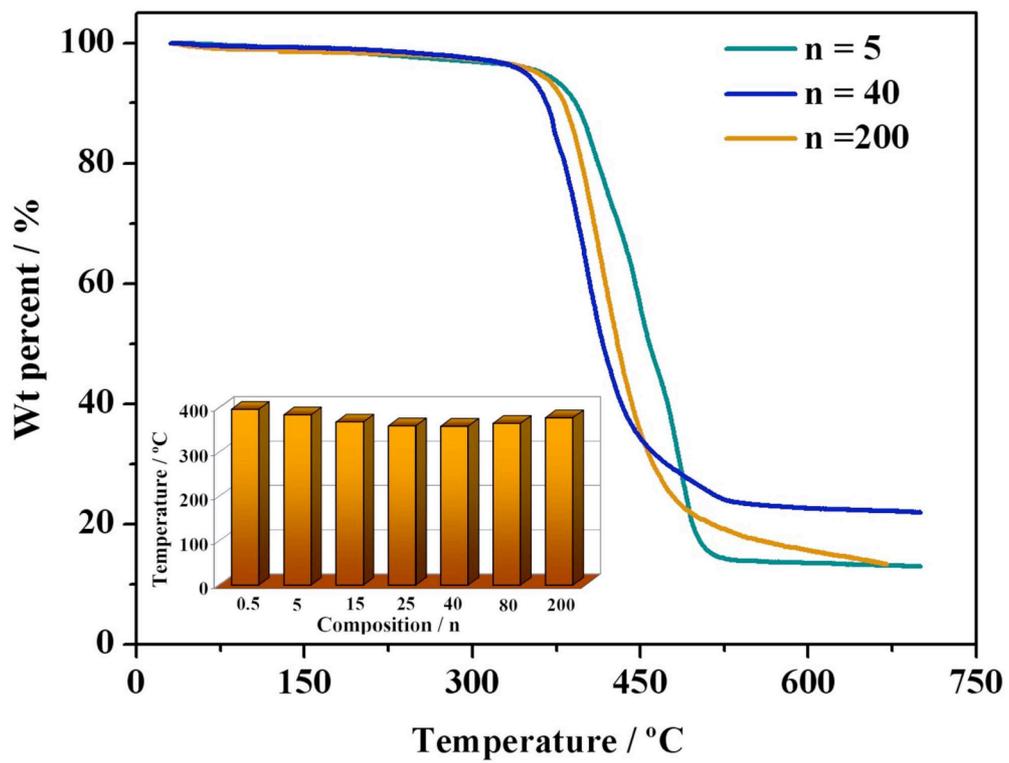


Figure 2

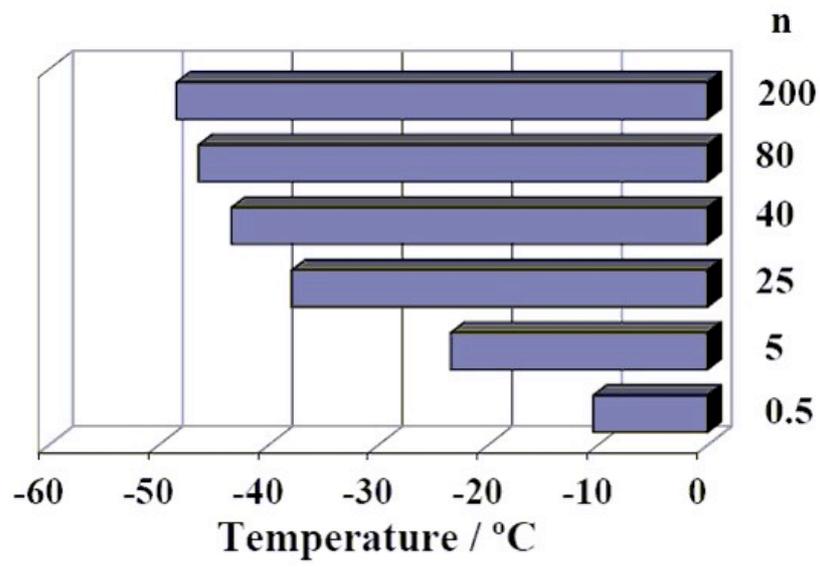


Figure 3

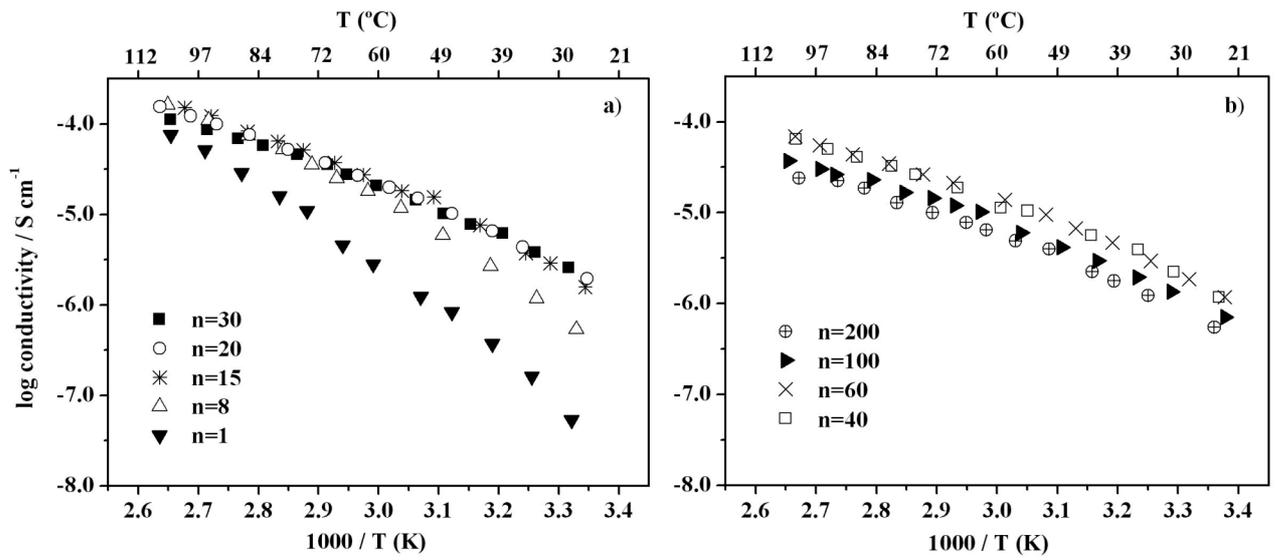


Figure 4 a) and b)

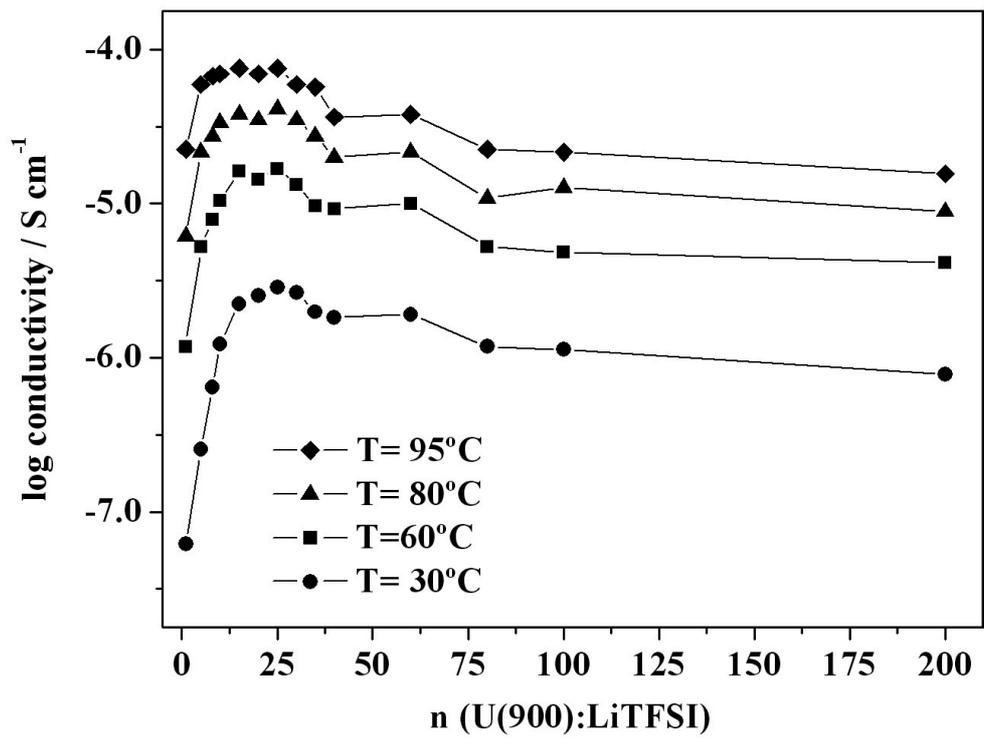


Figure 5

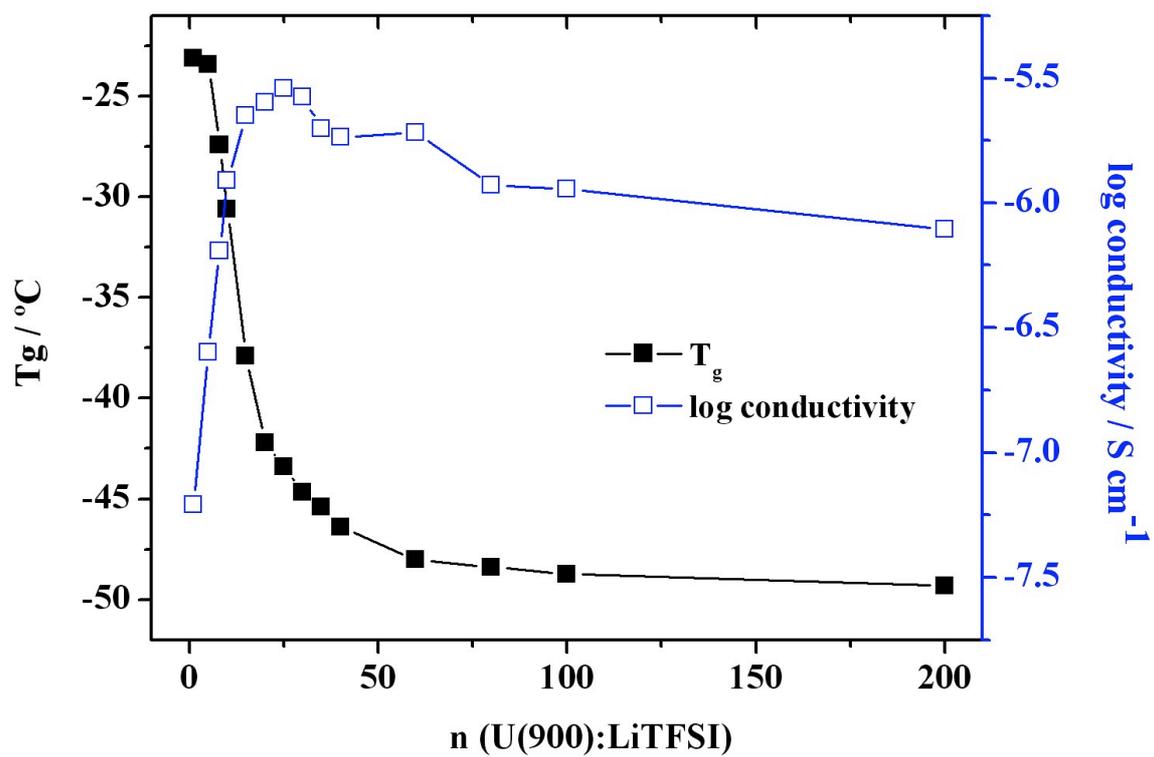


Figure 6

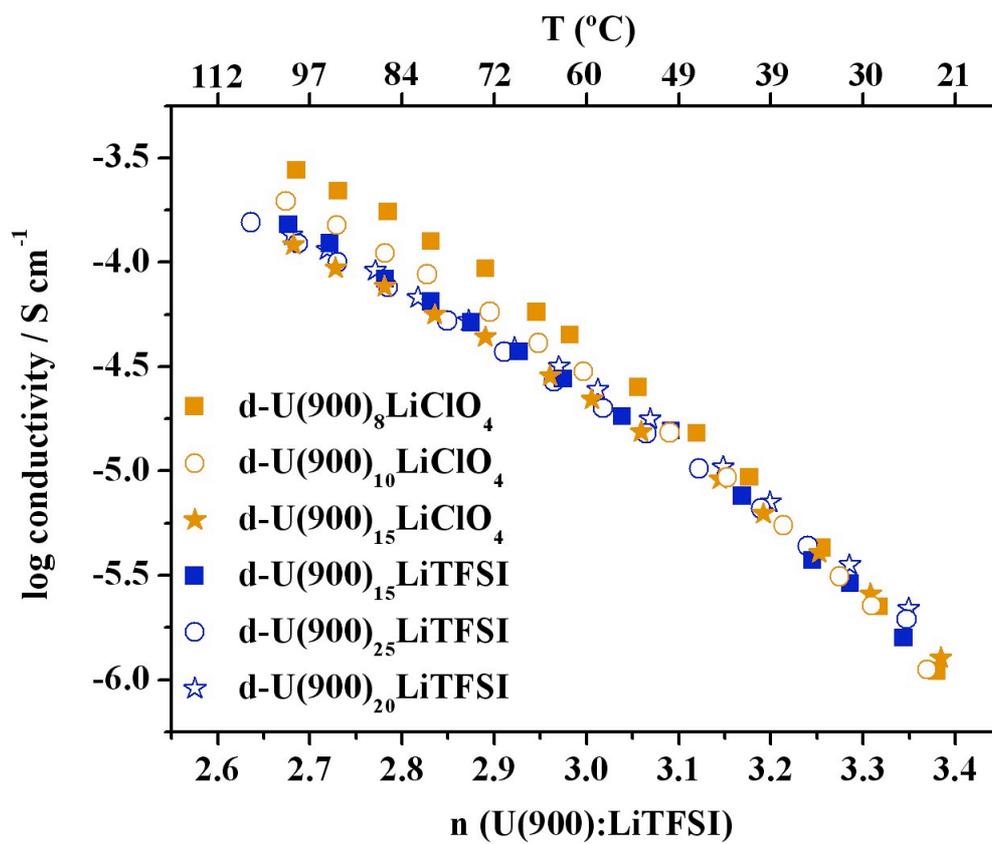


Figure 7

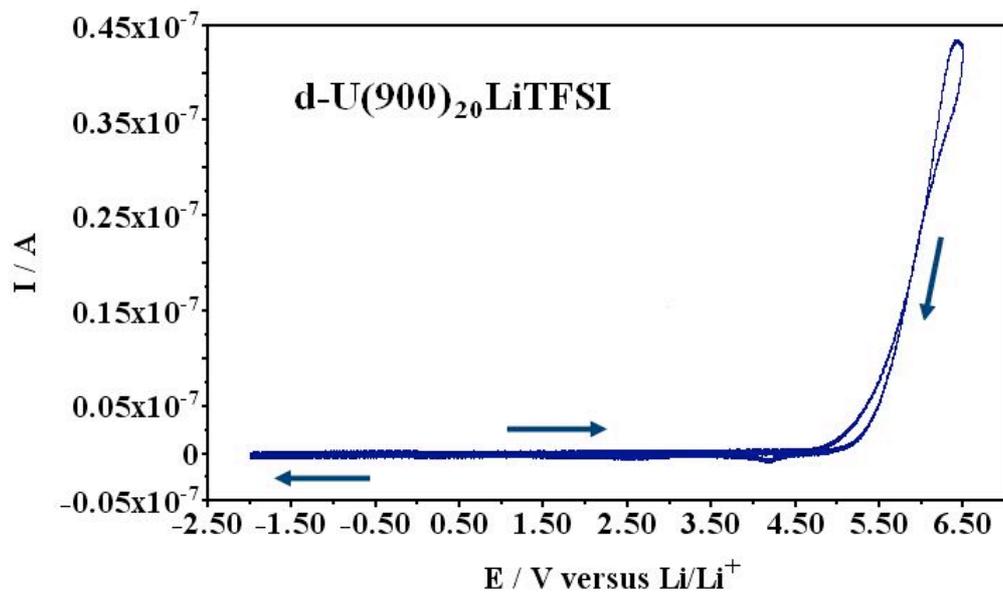


Figure 8

