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Sol-gel derived Li⁺-doped poly(ϵ -caprolactone)/siloxane biohybrid electrolytes

Abstract Electrolytes based on a poly(ϵ -caprolactone) (PCL)/siloxane organic/inorganic host framework doped with lithium triflate (LiCF₃SO₃) were synthesized through the sol-gel process. In this biohybrid matrix short PCL chains are covalently bonded via urethane linkages to the siliceous network. Samples with salt composition n (molar ratio of PCL repeat units per Li⁺ ion) ranging from ∞ to 0.5 were investigated. All the ormolyte materials analyzed are amorphous. Xerogels with $n > 0.5$ are thermally stable up to about 300 °C. The most conducting ormolyte of the series is that with $n = 0.5$ (1.6×10^{-7} and $3.2 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 25 and 100 °C, respectively).

Keywords sol-gel, poly(ϵ -caprolactone)/siloxane hybrid, ionic conductivity

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Introduction

Owing to their technological impact in the domain of solid state electrochemistry, in particular for the fabrication of advanced batteries, sensors and electrochromic and photoelectrochemical devices [1], polymer electrolytes [2] have attracted much interest in the past two decades.

Conventional polymer electrolytes are obtained through the dissolution of an ionic salt in a poly(oxyethylene) (POE)-type host polymer. Recently, the sol-gel process [3] emerged as a standard method for preparing improved polymer/siloxane electrolytes, since the organic/inorganic hybrid concept [4] allows to combine in a single material the amorphous character, the good mechanical resistance and the excellent thermal/chemical stability provided by the silica backbone, with the flexibility and solvating ability imparted by the POE chains. In addition, these modified host polymer systems withstand the addition of significantly higher amounts of guest salt than those usually permitted in the classical systems. Another advantage of this strategy is that the materials may be readily processed under mild conditions into thin films. Numerous Li^+ -doped ormolyte systems were investigated in the last few years [5-13].

In the present work we introduce a new family of di-urethane cross-linked siloxane-based hybrid electrolytes incorporating poly(ϵ -caprolactone) (PCL) segments (average molecular weight of 530 gmol^{-1}) and lithium triflate (LiCF_3SO_3). The structure, morphology, thermal properties and ionic conductivity of a series of samples with a wide salt concentration range will be investigated. To our knowledge, this is the first time that PCL is used for the purpose of developing ion conducting materials.

PCL is a linear, aliphatic thermoplastic, biocompatible, permeable, hydrophobic and biodegradable poly(ester), non-toxic for living organisms, that is resorbed after a certain period of implantation time. Because of this unique set of properties, this biopolymer and its

copolymers have found widespread application in the field of medicine, as biodegradable suture, artificial skin, resorbable prostheses and containers for sustained drug delivery [14-16]. In this context, PCL-based hybrid structures have been also developed. For instance, Tian et al. [17] produced PCL/silica ceramers that may find use as degradable bioglasses, as coating materials for bone implants and prosthetic devices and as supports for enzyme immobilization. A bioactive and degradable PCL/silica hybrid, with application as bone substitute, was also proposed by S-H. Rhee et al. [18] In both cases the average molecular weight of the PCL molecule employed was 2000 gmol^{-1} .

Experimental

Materials

Lithium trifluoromethanesulfonate (LiCF_3SO_3 , Aldrich) was dried under vacuum at $25 \text{ }^\circ\text{C}$ for several days prior to being used. α,ω -hydroxyl poly(ϵ -caprolactone) (PCL(530), Fluka, average molecular weight 530 g/mol) and 3-isocyanatepropyltriethoxysilane (ICPTES, Fluka) were used as received. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Merck) and tetrahydrofuran (THF, Merck) were stored over molecular sieves. High purity distilled water (H_2O) was used in all experiments.

Synthesis of the d-PCL(530)/siloxane biohybrids

The preliminary stage of the preparation of the LiCF_3SO_3 -doped d-PCL(530)/siloxane hybrids (where d stands for di) involved the formation of a urethane cross-link between the hydroxyl (-OH) end groups of the PCL chains and the isocyanate (-N=C=O) group of ICPTES to yield the organic-inorganic hybrid precursor designated as di-PCL(530)/siloxane precursor.

In the second stage of the synthetic procedure, a mixture of $\text{CH}_3\text{CH}_2\text{OH}$ and H_2O was added to the d-PCL(530)/siloxane precursor to promote the hydrolysis and condensation reactions characteristic of the sol-gel process. In the case of the preparation of the doped biohybrids, LiCF_3SO_3 was added to the $\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ solution.

A typical synthetic procedure follows:

Step 1 - Synthesis of the d-PCL(530)/siloxane precursor (Scheme 1): A mass of 2.000 g (3.774 mmol) of PCL(530) was dissolved in 10 ml of THF by stirring. A volume of 1.863 ml (7.548 mmol) of ICPTES was added to this solution under stirring in a fume cupboard. The flask was then sealed and the solution was stirred for approximately 24 h at 60-70 °C. The grafting process was infrared monitored. During the formation of the urethane groups, the intensity of the strong and sharp band characteristic of the stretching vibration of the $-\text{N}=\text{C}=\text{O}$ group of ICPTES, typically located at 2273 cm^{-1} , was progressively reduced, until it disappeared upon completion of the reaction. In parallel, a series of new bands, associated with the vibrations of the urethane group, appeared in the $1800\text{-}1500\text{ cm}^{-1}$ spectral region. The d-PCL(530)/siloxane precursor was obtained as a yellowish transparent oil. Its structure, represented in Scheme 2, was confirmed by ^{13}C NMR (CDCl_3 , 100.62 MHz) (Table 1).

Step 2 - Synthesis of the PCL(530)/siloxane biohybrid (Scheme 1): A volume of 1.761 ml (30.192 mmol) of $\text{CH}_3\text{CH}_2\text{OH}$, 204 μl (11.32 mmol) of H_2O and an appropriate mass of LiCF_3SO_3 were added to the THF solution of the d-PCL(530)/siloxane precursor obtained in the previous step. The mixture were stirred in a sealed flask for 30 min and then cast in a Teflon mould, which was covered with Parafilm and left in a fume cupboard for 24 h. The mould was transferred to an oven at 50 °C and the sample was aged for a period of 4 weeks. The materials were obtained as transparent, flexible monoliths with a yellowish hue. The ormolytes were identified using the notation d-PCL(530)_nLiCF₃SO₃, where n (salt composition) indicates the number of $(\text{C}(\text{=O})(\text{CH}_2)_5\text{O})$ PCL repeat units per Li^+ ion. Samples

with $n = \infty, 200, 93, 19, 2.3, 1$ and 0.5 were produced. Some relevant details of the synthetic procedure are given in Table 2.

Characterisation

^{13}C NMR spectra were recorded on a Brüker ARX400 NMR spectrometer (100.62 MHz) in CDCl_3 at CACTI - Universidade de Vigo (Spain). Chemical shifts, δ , are quoted in ppm from tetramethylsilane (TMS). ^{29}Si magic-angle spinning (MAS) and ^{13}C cross-polarization (CP) MAS NMR spectra were performed using a Brüker Avance 400 (9.4 T) spectrometer at 79.49 and 100.62 MHz, respectively. ^{29}Si MAS NMR spectra were recorded with $2 \mu\text{s}$ (equivalent to 30°) rf pulses, a recycle delay of 60 s and at a 5.0 kHz spinning rate. ^{13}C CP/MAS NMR spectra were recorded with $4 \mu\text{s}$ ^1H 90° pulse, 2 ms contact time, a recycle delay of 4 s and at a spinning rate of 8 kHz. Chemical shifts (δ) are quoted in ppm from TMS.

The X-ray diffraction (XRD) measurements were carried out at room temperature (RT) with a Rigaku Geigerflex D/max-c diffractometer system using monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) over the 2θ range of between 4 and 80° at a resolution of 0.05° . The xerogel samples, analyzed as solids, were not submitted to any thermal pre-treatment.

A DSC131 Setaram Differential Scanning Calorimeter was used to determine the thermal characteristics of the ormolytes. Disk sections with masses of approximately 30 mg were removed from the di-ureasil film, placed in $40 \mu\text{l}$ aluminium cans and stored in a dessicator over phosphorous pentoxide (P_2O_5) for one week at RT 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 $10^\circ\text{C min}^{-1}$. The purge gas used in both experiments was high purity nitrogen supplied at a constant $35 \text{ cm}^3 \text{ min}^{-1}$ flow rate.

Samples for thermogravimetric studies were transferred to open platinum crucibles and analysed using a Mettler TGA/SDTA 851 thermobalance at a heating rate of $10^{\circ} \text{ min}^{-1}$ using dried nitrogen as purging gas (20 ml/min). Prior to measurement, the xerogels were vacuum-dried at 80° C for about 48 h and kept in an argon-filled glove box.

For bulk conductivity measurements, an ormolyte disk was placed between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, > 99.9%). The electrode/ormolyte/electrode assembly was secured in a suitable constant volume support. The cell support was installed in a Buchi TO51 tube oven and a type K thermocouple placed close to the electrolyte disk measured the sample temperature. Bulk conductivities of the samples were obtained during heating cycles using the complex plane impedance technique (Schlumberger Solartron 1250 frequency response analyser and 1286 electrochemical interface) over a temperature range of between 25 and 100° C and at approximately 7° C intervals. Prior to characterization, the di-ureasil ormolytes were vacuum-dried at 80° C for about 48 h and kept in an argon-filled glove box.

Results and Discussion

Structure and Morphology

The ^{13}C CP/MAS and ^{29}Si MAS NMR spectra of selected d-PCL(530)_nLiCF₃SO₃/siloxane hybrids are reproduced in Figs. 1 and 2, respectively. The position and attribution of the resonance peaks [19-25] are listed in Tables 1 and 3, respectively.

The ^{13}C CP/MAS NMR spectra of the urethane cross-linked d-PCL(530)/siloxane xerogels with $n = \infty$, 93 and 2.3 is dominated by a series of peaks attributed to the resonance of the methylene carbon atoms of the PCL repeat units (see carbon atoms C⁶ to C¹⁰ in Table 1 and Fig. 1). The peaks associated with the carbonyl carbon atoms of the ester (C(=O)OCH₂)

and urethane (NHC(=O)O) groups are ill-defined and weak (see carbons C¹⁴ and C¹³ in Table 1, respectively, and Fig.1). The characteristics peaks of the propyl carbon atoms of the -Si-(CH₂)₃-N moieties are present in the ¹³C CP/MAS NMR spectra of all the three samples (see carbons C¹, C² and C³ in Table 1 and Fig. 1), a proof that the grafting reaction was not accompanied by the rupture of bonds in the Si-propyl segments. The absence in the ¹³C CP/MAS NMR spectrum of the hybrid material with n=93 of the peaks due to the ethoxy carbon atoms (see carbons C⁴ and C⁵ in Table 1 and Fig.1) provides solid evidence that the hydrolysis reaction went to completion.

It may be inferred from Fig. 2 that the ²⁹Si MAS NMR spectra of the d-PCL(530)-based xerogels with n = ∞, 93 and 2.3 display peaks at approximately -50, -58 and -66 ppm (Table 3). These signals are assigned to T₁ (CH₂-Si(OR)₂(OSi)), T₂ (CH₂-Si(OR)(OSi)₂) and T₃ (CH₂-Si(OSi)₃) sites, respectively (Note: according to the conventional T_m silicon (Si) notation, m* = 1, 2 and 3 is the number of Si atoms bonded to O-Si units). The polycondensation rates c (where c = 1/3 (%T₁ + 2%T₂ + 3%T₃)) calculated for the d-PCL(530)/siloxane doped materials are significantly higher than that of the non-doped framework and suffer an increase with the increase of salt concentration. The empirical formula deduced for the three samples examined is given in Table 3. Based on the conclusions retrieved from the analysis of the ¹³C CP/MAS NMR spectrum of the xerogel d-PCL(530)₉₃LiCF₃SO₃, we associate the residual OR groups in the T₁, T₂ and T₃ site formula indicated above to non-reacted -OH groups (Table 3), a clear indication that the final material contains residual silanol groups (-Si-OH).

The XRD patterns and the DSC thermograms of the d-PCL(530)_nLiCF₃SO₃ samples illustrated in Figs. 3 and 4, respectively, indicate that the materials investigated are entirely amorphous. The broad band, Gaussian in shape, centered at approximately 21.98° in the diffractograms all the biohybrids is associated with the coherent diffracting domains of the

* The classical notation T_n has been changed to T_m, to avoid any confusion with the notation n used for salt composition throughout the text.

siliceous backbone [26]. The weak band distinguished at approximately 44° in the diffractogram of the samples with $n \geq 1$ is tentatively associated with the second-order of the peak centred near 21.98° .

The TGA curves of representative urethane cross-linked d-PCL(530)_nLiCF₃SO₃ composites are depicted in Fig. 5. These data demonstrate that the thermal decomposition of the doped materials with $n > 0.5$ is initiated at temperatures higher than 300°C . The presence of the guest salt appears to destabilise the hybrid host structure in a non-oxidising atmosphere. In the case of the less concentrated d-PCL(530)_nLiCF₃SO₃ samples with $n = 200$ and 93 , a unique mass loss (gradual) is detected in the curves (onset at approximately 300°C). In contrast, in the hybrids with $n = 19$, 2.3 and 0.5 we observe a three mass loss degradation process.

Ionic conductivity

The examination of the Arrhenius conductivity plots of the doped d-PCL(530)_nLiCF₃SO₃ xerogels illustrated in Fig. 6(a) reveals that the most conducting ormolyte over the temperature range of temperatures considered is PCL(530)_{0.5}LiCF₃SO₃ (4.0×10^{-6} , 1.0×10^{-5} and $6.74 \times 10^{-5} \Omega^{-1}\text{cm}^{-1}$ at 35 , 50 and 104°C , respectively).

The conductivity isotherms included in Fig. 6(b) distinctly show the presence of a conductivity maximum at $n = 2.3$. Further studies involving the measurement of the ionic conductivity of more concentrated ormolytes are needed to determine the location of other conductivity maxima, as it is not clear at the present stage if composition $n = 0.5$, which leads to higher conductivity than $n = 2.3$, corresponds to a second conductivity maximum.

Conclusions

LiCF₃SO₃-doped d-PCL(530)/siloxane biohybrid ormolytes were synthesized by the sol-gel process. Samples with $\infty > n \geq 0.5$ were produced as amorphous, flexible, thin monoliths. The materials with $n > 0.5$ are thermally stable up to 300 °C. The d-PCL(530)_{0.5}LiCF₃SO₃ compound displays the highest ionic conductivity over the range of temperatures analyzed (approximately 4.0×10^{-6} and $6.7 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 35 and 104 °C, respectively). The encouraging results obtained suggest that further research on this type of system is worth pursuing.

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Fig. 1 ^{13}C CP/MAS NMR spectra of selected d-PCL(530)_nLiCF₃SO₃/siloxane hybrids.

Fig. 2 ^{29}Si MAS NMR spectra of selected d-PCL(530)_nLiCF₃SO₃/siloxane hybrids.

Fig. 3 XRD patterns of selected d-PCL(530)_nLiCF₃SO₃/siloxane hybrids.

Fig. 4 DSC curves of the d-PCL(530)_nLiCF₃SO₃/siloxane hybrids.

Fig. 5 TGA curves of selected d-PCL(530)_nLiCF₃SO₃/siloxane hybrids.

Fig. 6 Arrhenius conductivity plot (a) and isotherms of the ionic conductivity versus composition (b) of the d-PCL(530)_nLiCF₃SO₃/siloxane hybrids.

Tables

Table 1 ^{13}C CP/MAS data of selected d-PCL(530)_nLiCF₃SO₃/siloxane hybrids.

Table 2 Details of the synthetic procedure of the d-PCL(530)_nLiCF₃SO₃/siloxane hybrids.

Table 3 ^{29}Si MAS/NMR data of selected d-PCL(530)_nLiCF₃SO₃/siloxane hybrids.

Scheme

Scheme 1 Synthetic procedure of the d-PCL(530)_nLiCF₃SO₃/siloxane hybrids.

Scheme 2 Structure of the d-PCL(530)_nLiCF₃SO₃/siloxane hybrid precursor.

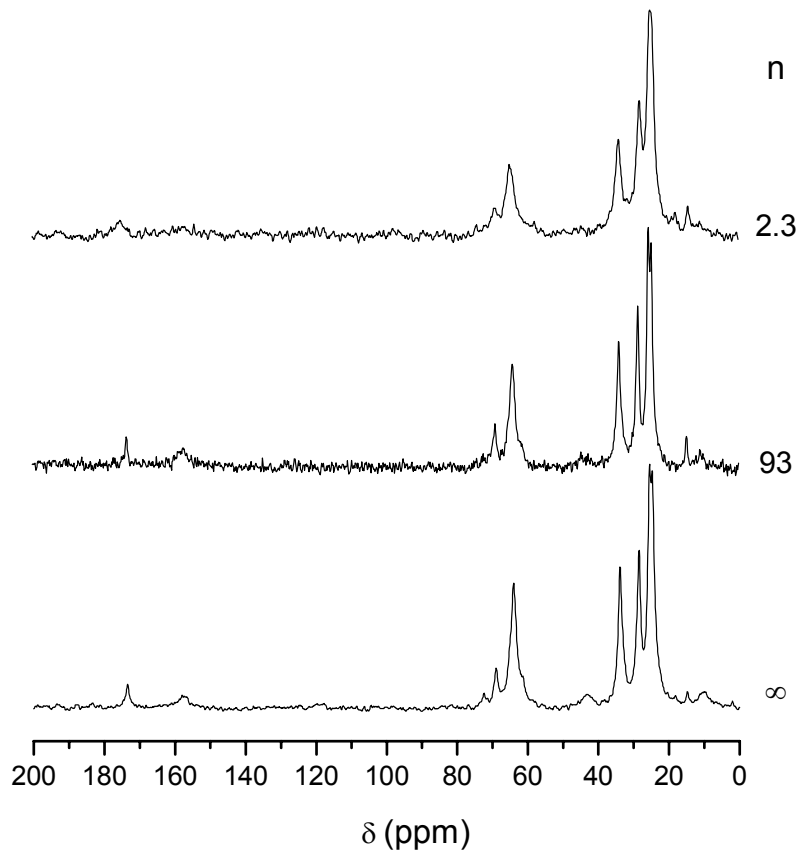


Fig. 1, S. C. Nunes et al., *Journal of Solid State Electrochemistry*

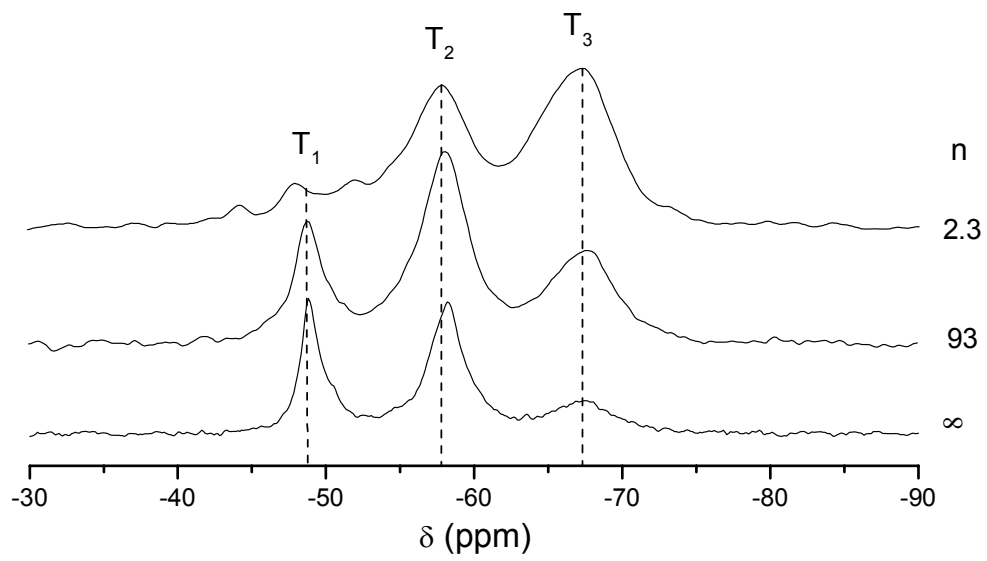


Fig. 2, S. C. Nunes et al., *Journal of Solid State Electrochemistry*

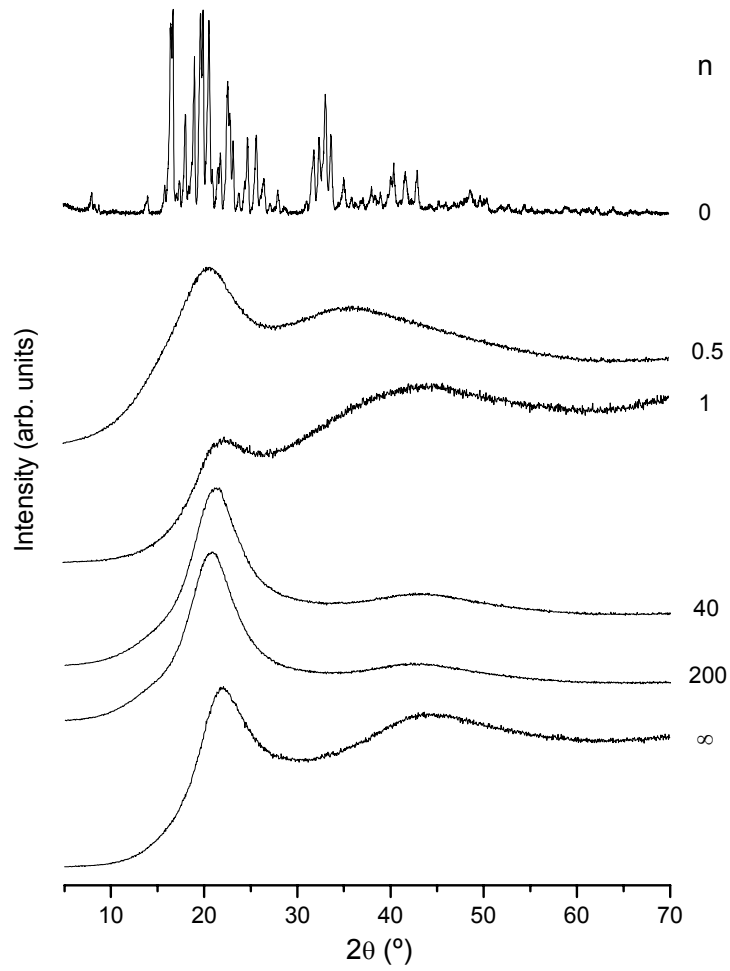


Fig. 3, S. C. Nunes et al., *Journal of Solid State Electrochemistry*

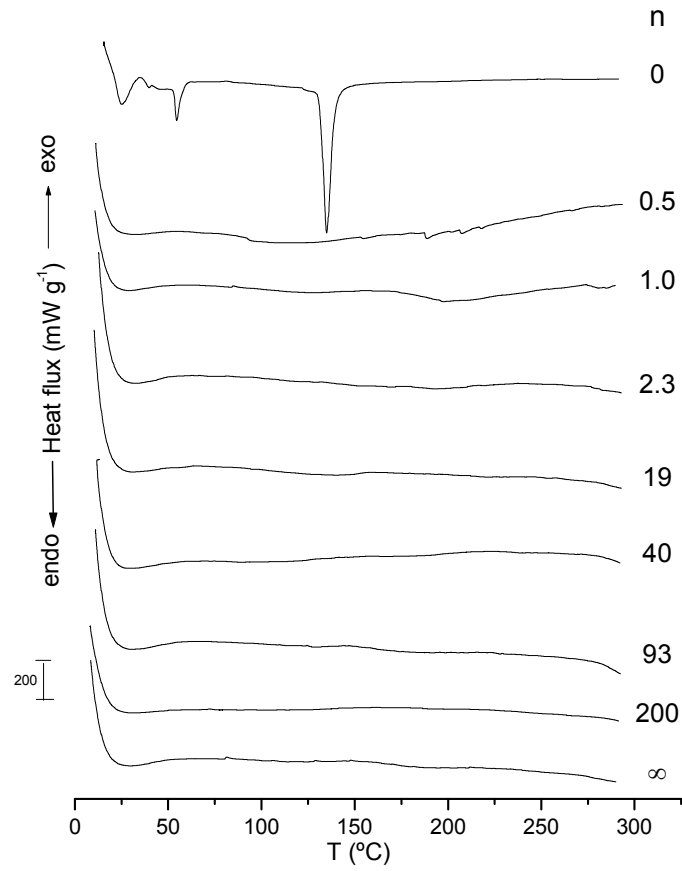


Fig. 4, S. C. Nunes et al., *Journal of Solid State Electrochemistry*

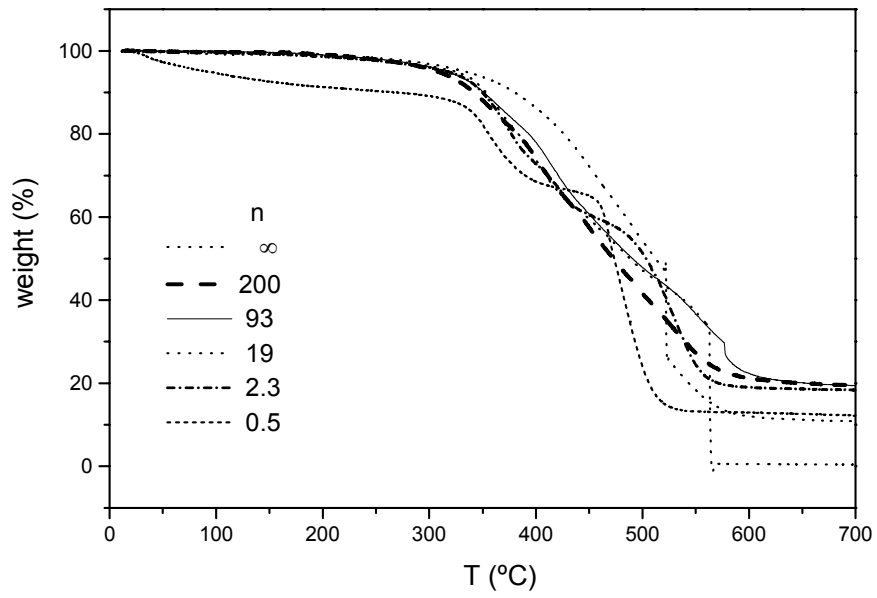
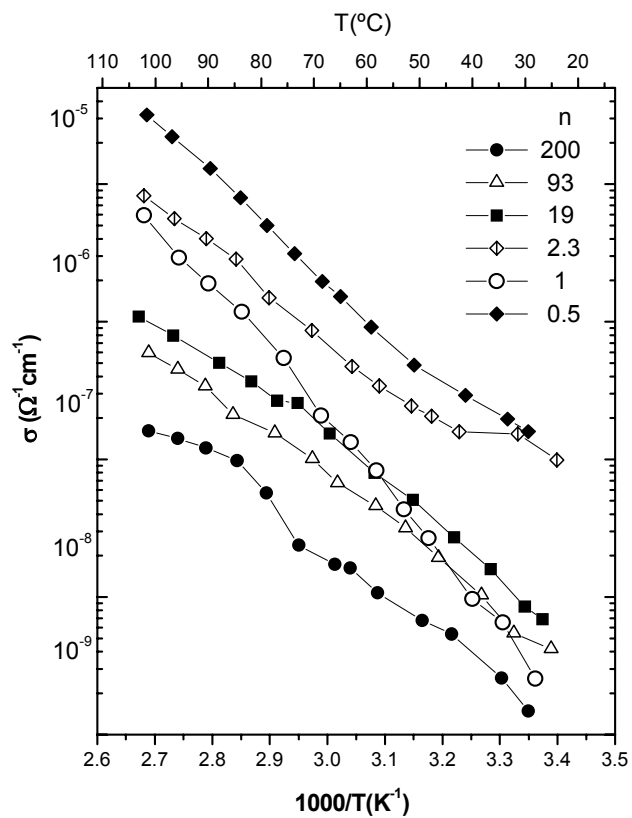
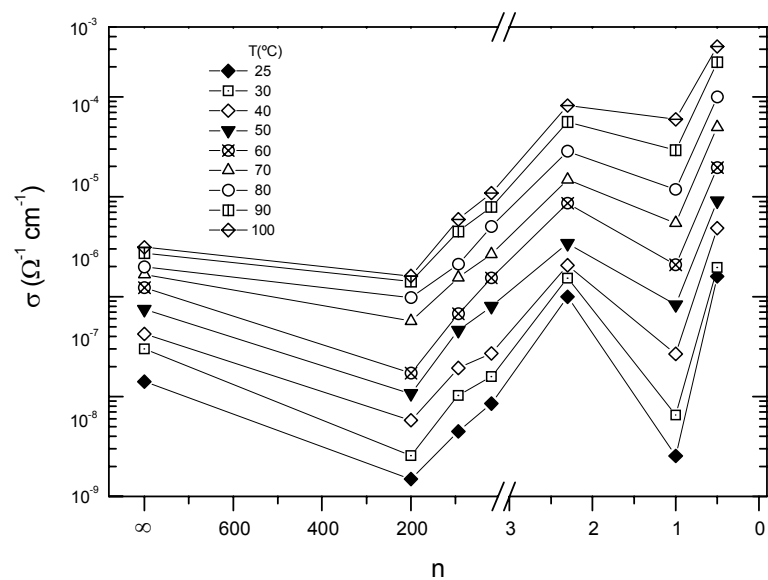


Fig. 5, S. C. Nunes et al., *Journal of Solid State Electrochemistry*



(a)



(b)

Fig. 6, S. C. Nunes et al., *Journal of Solid State Electrochemistry*

Table 1, S. C. Nunes et al., *Journal of Solid State Electrochemistry*

¹ H NMR d-PCL(530)/siloxane precursor		Attribution		¹³ C NMR d-PCL(530)/siloxane precursor	¹³ C CP/MAS NMR d-PCL(530) _n LiCF ₃ SO ₃			Attribution [19-25]
					∞	93	2.3	
5.20-5.10	s, b	2H	H ^m	173.11-172.91	173.39	173.38	175.20	C ¹⁴
4.20-4.00	m	4H	H ^k	156.40	157.30	157.32	158.00	C ¹³
4.00-3.80	m	≅ 7.4H	H ^f	68.65-68.61	69.00	68.93	69.00	C ¹²
3.67-3.61	q	12H	H ^d	63.94-63.67	64.06	64.03	64.91	C ⁶
3.53-3.43	m	4H	H ^l	62.95-62.87	61.51	62.32	62.00	C ¹¹
3.05-2.97	m	4H	H ^c	57.98	55.90	-	57.76	C ⁴
2.19-2.11	m	≅ 7.4H	H ^j	43.06-42.99	43.03	44.20	44.60	C ³
1.53-1.42	m	≅ 19.4H	H ^b , H ⁱ , H ^g	33.71-33.57	33.92	33.86	34.00	C ¹⁰
1.25-1.20	m	≅ 7.4H	H ^h	28.3	28.47	28.44	28.04	C ⁷
1.06-1.03	t	18 H	H ^e	25.12-25.08	25.40	25.46	25.15	C ⁹
0.47-0.43	t	4H	H ^a	24.23-24.07	24.81	24.71	23.80	C ⁸
				22.89	20.38	20.96	20.30	C ²
				17.93-17.86	18.17	-	17.83	C ⁵
				7.23	14.85	14.63	14.30	C ¹
					9.99	10.83		

s - singlet, t - triplet, q - quartet, m - multiplet, b - broad

Table 2, S. C. Nunes et al., *Journal of Solid State Electrochemistry*

$n = [\text{C}(=\text{O})(\text{CH}_2)_5\text{O}]/\text{Li}^+$	$m(\text{LiCF}_3\text{SO}_3)$	Si/Li^+	Si/Li^+
$/\text{molmol}^{-1}$	$/\text{g}$	$/\text{molmol}^{-1}$	$/\text{gg}^{-1}$
∞	-	-	-
200	0.0109	107.527	170.491
93	0.0235	50.0000	79.2781
40	0.0547	21.5054	34.0981
19	0.1153	10.2150	16.1966
2.3	0.9523	1.2365	1.9606
1.0	2.1903	0.5376	0.8524
0.5	4.3805	0.2688	0.4262

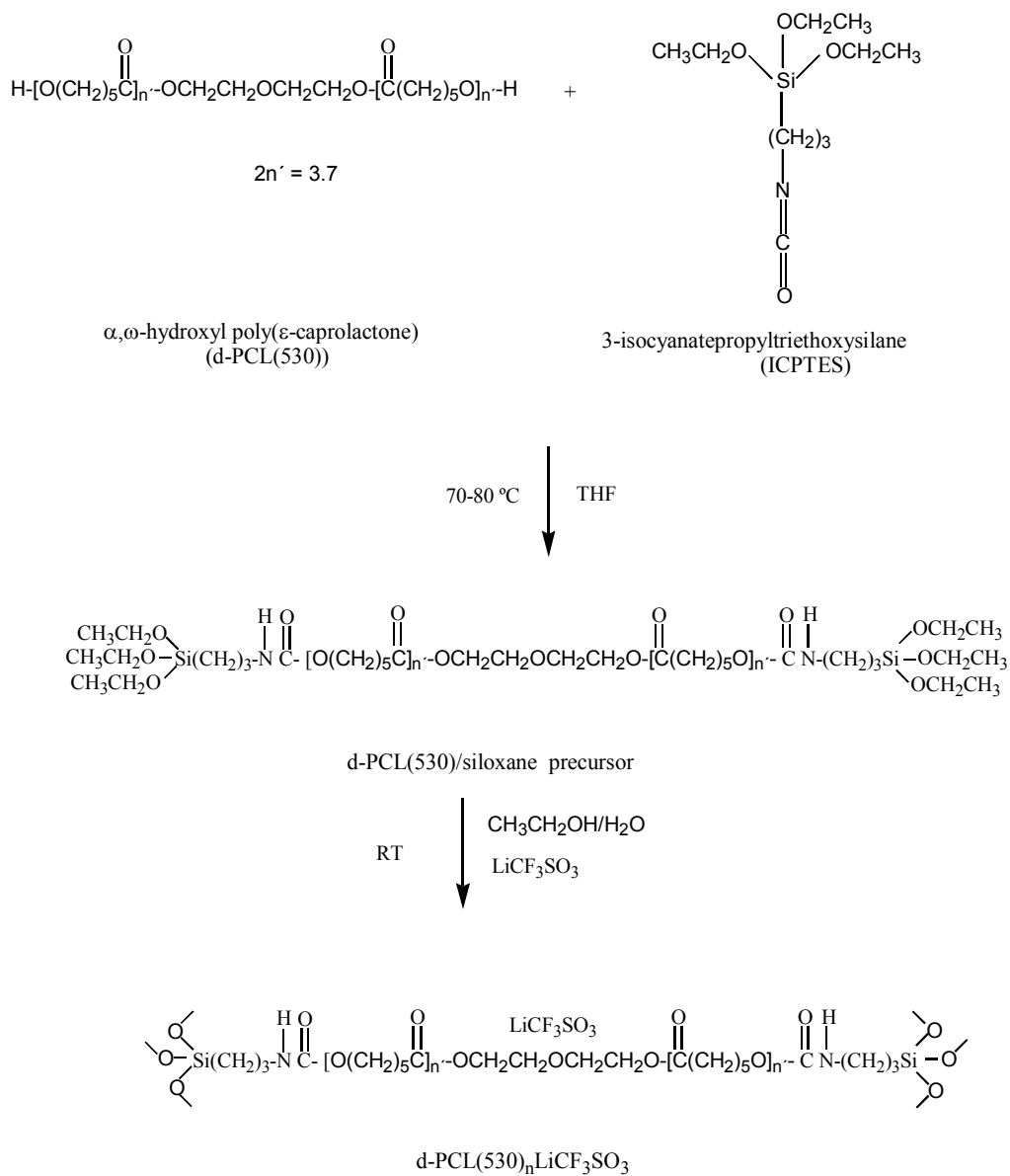
Table 3, S. C. Nunes et al., *Journal of Solid State Electrochemistry*

²⁹ Si MAS NMR						
n	T ₁ (CH ₂ -Si(OSi)(OR) ₂) (%)	T ₂ (CH ₂ -Si(OSi) ₂ (OR)) (%)	T ₃ (CH ₂ -Si(OSi) ₃) (%)	c (%)	Empirical formula	
∞	-49.1 (33.5)	-58.1 (52.9)	-66.6 (13.6)	60	R' _{0.5} Si (OR) _{0.9} (O) _{1.2}	
93	-48.9 (20.0)	-58.0 (56.1)	-66.0 (23.0)	67	R' _{0.5} Si (OH) _{1.0} (O) _{1.0}	
2.3	-51.2 (11.9)	-57.4 (35.6)	-66.9 (52.5)	80	R' _{0.5} Si (OR) _{0.6} (O) _{1.2}	

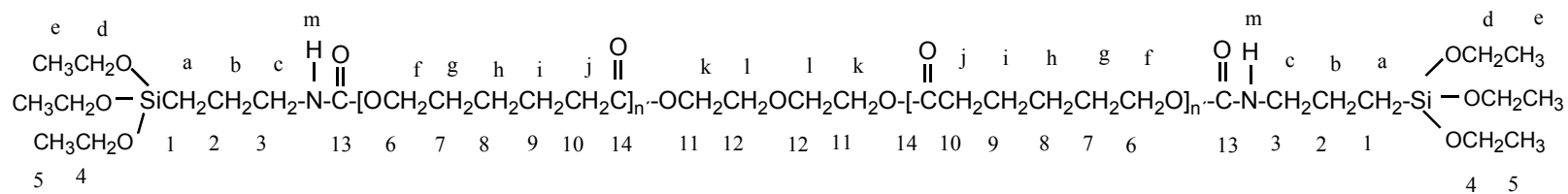
Note: R' = -(CH₂)₃-NH-C(=O)-[O(CH₂)₅C(=O)]_n-(OCH₂CH₂OCH₂CH₂O)-(C(=O)(CH₂)₅O)_n-C(=O)-NH-(CH₂)₃-

R = CH₂CH₃ or H

Scheme 1: S. Nunes et al, *Journal of Solid State Electrochemistry*



Scheme 2, S. Nunes et al., *Journal of Solid State Electrochemistry*



$$2n' = 3.7$$