

Supporting Information for:

Single-ion conductor nanostructured organic-inorganic hybrid membranes for lithium batteries

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Materials and methods

Materials

Polyethylene Oxide ($M_n = 1\,000\text{ g.mol}^{-1}$) was obtained from Alfa Aesar and dried under vacuum at 70°C during 12 hours before use. 3-Isocyanatopropyltriethoxysilane was obtained from ABCR. 2-(4-chlorosulphonylphenyl)ethyl trimethoxysilane (50% wt in dichloromethane) was purchased from Acros, pentane, lithium chloride and propylene carbonate from Aldrich and ethanol from VWR. THF and triethylamine were distilled before use.

TGA

Thermal Gravimetric Analyses were carried out on a Netzsch STA 409 PC apparatus at 5°C min^{-1} under air between 25°C and 800°C and using ca. 10 mg samples in alumina crucible.

DSC

The membranes calorimetric measurements were performed with NETSCH Instrument DSC 204-F1. Differential Scanning Calorimetry (DSC) thermograms were recorded on raising the temperature from -110 to 150°C at a heating rate of 10°C/min under nitrogen atmosphere.

IR

Fourier Transform Infrared (FTIR) spectra with Attenuated Total Reflectance (ATR) were recorded in the $4000\text{--}400\text{ cm}^{-1}$ range, using 32 scans at a nominal resolution of 4 cm^{-1} , by means of an AVATAR 320 FTIR spectrometer.

Liquid-state ^1H , ^{13}C and ^{29}Si NMR

^1H , ^{13}C and ^{29}Si liquid-state NMR were recorded on a Bruker DRX 300 spectrometer at room temperature. Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks (CdCl_2 : $\delta\,7.26\text{ ppm } ^1\text{H}$; $\delta\,77.16\text{ ppm } ^{13}\text{C}$). Coupling constants (J) are reported in Hz.

Solid-state ^{29}Si NMR

^{29}Si Solid-state NMR spectra referenced to tetramethylsilane (TMS), were recorded at 7.05 T on a Varian VNMRs 300 MHz spectrometer, using a 7.5 mm MAS probe spinning at 5 kHz.

Single-pulse sequences with continuous-wave ^1H decoupling were used, with $2\ \mu\text{s}$ $\pi/2$ pulse duration and a recycle delay of 60 s.

Percentages of T1 (-49 ppm), T2 (-58 ppm), and T3 (-66 ppm) silicon environments were estimated using DMFIT 2009 (**Table S2**).³ After deconvolution, the condensation ratios were estimated from integrated signals with the following formula:

$$\text{Condensation ratio}(\%) = \frac{3 * T3 + 2 * T2 + T1}{3}$$

Table S1: T1, T2 and T3 percentages from solid-state ^{29}Si NMR spectra using deconvolution with DMFIT 2009

	T₁ (%)	T₂ (%)	T₃ (%)
Li-free	6.6	15.6	77.8
EO/Li-30	-	45.7	54.3
EO/Li-20	-	30.4	69.6
EO/Li-10	-	30.2	69.8

WAXS

The Wide Angle X-ray Scattering (WAXS) experiments were conducted on a device equipped with a copper rotating anode ($\lambda = 1.54\ \text{\AA}$) (Rigaku Corporation, Tokyo, Japan), a Gobel's mirrors collimation system (ELEXIENCE, Verrières le Buisson, France) and a two-dimensional detector (Princeton Instrument SCX2D, Trenton, NJ, USA). The distance between sample and detector was set at 55 mm and the exposure time was set at 300 seconds. Since no attempt was made to ensure a constant thickness of sample in the x-ray beam, absolute intensity comparisons of the patterns for different samples is not warranted. For all patterns the background signal was subtracted.

DMA

The thermo-mechanical response of the material was evaluated through Dynamic Mechanical Analysis (DMA) using a homemade apparatus in torsion mode at 1 Hz and 10^{-2} rad angle with a heating rate of $1\ \text{K min}^{-1}$ from $-180\ \text{C}$ to $90\ \text{C}$. Samples were typically 20 mm long (the distance between grips was then 10 mm), 3 mm wide and 0.35–0.45 mm thick. The analysis output was the variation of the complex shear modulus $G^* = G' + i.G''$ with temperature. The temperature at the maximum of loss modulus (G'') is defined as the

mechanical main relaxation temperature. It is worth recalling that molecular mobility is related to the position of the loss modulus peak and not to the loss factor ($\tan \delta$), which depends on both the mobility and the storage modulus as $\tan \delta = G''/G'$.⁴

Syntheses

Synthesis of bis-silylated (PEO)^{1,2}

8.90 g of 3-isocyanatopropyltriethoxysilane (0.036 mol) were added dropwise at room temperature under argon to a solution of 12 g of dry PEG 1000 (0.012 mol) and 4.0 mL of triethylamine (0.028 mol) in dry THF (30 mL). The resulting mixture was stirred under reflux for 72h. After evaporation of the solvent, the crude product was washed with pentane (50 mL×3), then dried under vacuum, affording 16.44 g (0.011 mol, 93%) of a slightly yellow viscous liquid.

¹H NMR (300 MHz, CDCl₃): 0.55 (t, $J = 9\text{ Hz}$, 4H, CH_2Si), 1.16 (t, $J = 9\text{ Hz}$, 18H, $\text{CH}_3\text{CH}_2\text{OSi}$), 1.54 (m, 4H, $\text{CH}_2\text{CH}_2\text{NH}$), 3.11 (q, $J=9\text{ Hz}$, 4H, CH_2NH), 3.58 (s, 80H, $\text{CH}_2\text{CH}_2\text{O}$), 3.73 (q, $J=9\text{ Hz}$, 12H, $\text{CH}_3\text{CH}_2\text{OSi}$), 4.14 (t, $J = 9\text{ Hz}$, 4H, CH_2OC), 5 (s, 2H, NH)
¹³C NMR (75.5 MHz, CDCl₃): 7.6 (s, CH_2Si), 18.3 (s, $\text{CH}_3\text{CH}_2\text{OSi}$), 23.3 (s, $\text{CH}_2\text{CH}_2\text{Si}$), 43.4 (s, CH_2NH), 57.8 (s, $\text{CH}_3\text{CH}_2\text{OSi}$), 63.8 (s, $\text{CH}_2\text{CH}_2\text{O}$), 70.5 (s, CH_2OCO); 156.5 (s, OCO)

²⁹Si NMR (40 MHz, CDCl₃): -45.7

IR (ν , cm⁻¹, ATR): 1715 ($\nu_{\text{C=O}}$), 3345 ($\nu_{\text{N-H}}$), 1074 ($\nu_{\text{C-O}}$)

Preparation of membranes

Membranes were prepared by dissolving the bis-silylated PEO and 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane precursor in ethanol with 10 equivalents of acidic water (pH 1.5). The resulting solution was stirred for 24 hours and then poured in a Teflon vial. Solvent evaporation took place in a temperature and humidity controlled chamber (30°C, 30% humidity). The resulting membranes were dried under vacuum at 90°C for 2 hours and then washed with ethanol by means of Soxhlet extractor for 24 hours. The membranes were then placed in a 2 M LiCl solution in ethanol for 4 days. After the lithiation step, the membranes were washed again with ethanol by means of Soxhlet extractor for 24 hours and

dried under vacuum at 90°C for 2 hours. Finally, the membranes were stored in a glove box under argon.

IR (v, cm⁻¹, ATR) : 1030-1010 (v_{S=O})

Table S2: Weights and volumes used for each synthesis

	m _{PEG silylated} (mg)	m _{precursor} (mg)	V _{EtOH} (mL)	V _{acidic water} (mL)
EO/Li-30	350	116	7	0.3
EO/Li-20	350	176	7.5	0.3
EO/Li-10	350	344	9.2	0.3

Swelling of the membranes with propylene carbonate (PC)

The membranes were placed in an excess of propylene carbonate during 24 hours.

Assessment of complete lithiation by acid-base titration

Two-step synthesized membranes: SO₃H containing membranes were dipped in a volume of LiCl solution (2M) in ethanol. After 7 days, the membranes were removed and the amount of HCl released was measured by acid base titration, using NaOH solution (0.02M) and phenolphthalein as indicator.

One-step synthesized membranes: The membranes were dipped in a volume of LiCl solution (2M) in ethanol. After the removal of membranes, titrations using NaOH solution (0.02M) and phenolphthalein as indicator indicated a negligible residual HCl release.

Conductivity measurements

Conductivity measurements were performed on a potentiostat VSP-300 Biologic. The membranes were dried under vacuum overnight and placed in a Swagelok cell under argon atmosphere using a glovebox. Ionic conductivity was measured by electrochemical impedance spectroscopy on heating from 20 to 90°C with a range frequency from 10⁷ to 10⁻³ Hz. For each sample, two successive measurements were done to check the values. As an example, the Nyquist diagram of swelled membrane **EO/Li-10** at 60°C and the related graph of frequency vs. resistance are given here:

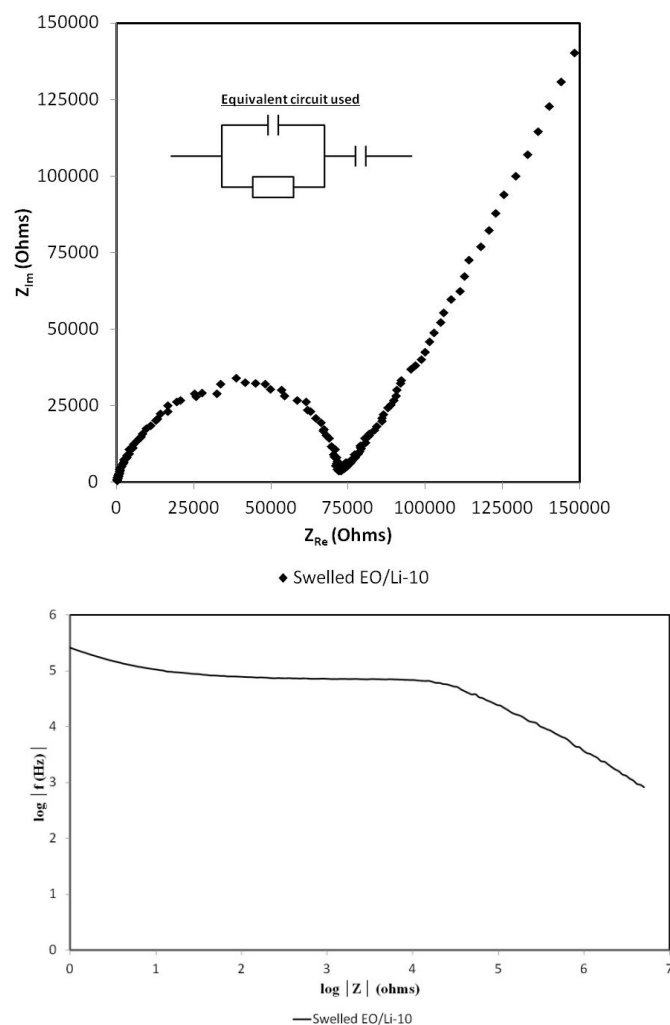


Figure S1: Nyquist diagram of swelled membrane **EO/Li-10** at 60°C (top) and related graph of frequency vs. resistance (bottom)

At least three sets of measurements (S/cm) were done for each EO/Li value. Some average conductivities are given in Table S3 with uncertainties.

Table S3: Uncertainties of conductivity measurements at 30, 60 and 90 °C

	EO/Li-30	EO/Li-20	EO/Li-10
30°C	$4,77\text{E}^{-9} \pm 3,21\text{E}^{-9}$	$1,62\text{E}^{-9} \pm 7,80\text{E}^{-10}$	$2,36\text{E}^{-9} \pm 6,00\text{E}^{-11}$
60°C	$4,91\text{E}^{-8} \pm 4,07\text{E}^{-8}$	$4,64\text{E}^{-8} \pm 1,47\text{E}^{-8}$	$3,48\text{E}^{-8} \pm 5,20\text{E}^{-9}$
90°C	$1,57\text{E}^{-7} \pm 1,08\text{E}^{-7}$	$2,37\text{E}^{-7} \pm 6,70\text{E}^{-8}$	$2,92\text{E}^{-7} \pm 3,60\text{E}^{-8}$
	Swelled EO/Li-30	Swelled EO/Li-20	Swelled EO/Li-10
30°C	$1,51\text{E}^{-7} \pm 1,00\text{E}^{-7}$	$4,97\text{E}^{-7} \pm 3,55\text{E}^{-7}$	$4,59\text{E}^{-7} \pm 7,80\text{E}^{-8}$
60°C	$8,22\text{E}^{-7} \pm 4,72\text{E}^{-7}$	$2,54\text{E}^{-6} \pm 1,70\text{E}^{-6}$	$4,55\text{E}^{-6} \pm 2,56\text{E}^{-6}$
90°C	$4,59\text{E}^{-7} \pm 7,80\text{E}^{-8}$	$1,89\text{E}^{-6} \pm 2,81\text{E}^{-7}$	$4,07\text{E}^{-6} \pm 4,50\text{E}^{-7}$

VTF equation: Pseudo-activation energies B related to the segmental motions of the polymer

were evaluated by using Vogel-Tamman-Fulcher model equation:
$$\sigma = \frac{A}{\sqrt{T}} \exp\left[\frac{-B}{k(T - T_0)}\right]$$

A and B were treated as fitting parameters, whereas the equilibrium glass transition temperature T_0 was settled at 50 °C below the glass transition temperature (T_g).

Table S4: VTF fit parameters of solvent-free membranes

	B (J/mol)	B(eV)	A (S.cm ⁻¹ .K ^{1/2})
EO/Li-30	6690	0.069	6.75 10 ⁻³
EO/Li-20	5710	0.059	3.77 10 ⁻³
EO/Li-10	3580	0.037	6.67 10 ⁻⁴

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