Electronic Supplementary Information

PVDF-HFP/ether-modified polysiloxane membranes obtained via airbrush spraying as a*ctive* separators for application in lithium ion batteries

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Experimental

Synthesis of side chain triethylene glycol allyl methyl ether **2** (PEO3)
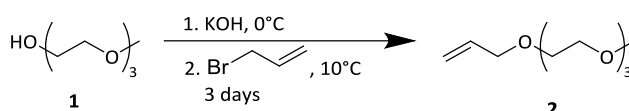

Fig. S1: Reaction scheme of the synthesis of triethylene glycol allyl methyl ether 2 (PEO3).

The synthesis of ethylene glycol allyl methyl ether **2** was done by a modified procedure of a literature instruction of BRESLOW and LIGHT.[1]

Alcohol **1** (263.0 mL, 275.6 g, 1.6 mol, 1.0 eq.) was presented in a 1 L triple-neck round-bottom flask with a mechanic stirrer and a dropping funnel and cooled down to 0 °C with an water/ice bath. KOH (102.1 g, 1.8 mol, 1.1 eq.) was added to the alcohol. After stirring for 1 h, allyl bromide (140.5 mL, 196.7 g, 1.6 mol, 1.0 eq.) was slowly added over the dropping funnel under cooling. After 3 d of stirring, the precipitated KBr was filtered off by a Büchner funnel and the filter cake was washed with *n*-hexane. The filtrate was dried over $MgSO_4$ and subsequently concentrated under diminished pressure. After distillation, the corresponding ethylene glycol allyl methyl ether **2** was obtained as a clear and colorless liquid (265.5 g, 1.3 mol, yield: 80%; bp.: 66-68 °C, 2.1×10^{-1} mbar).

GC-MS (CI): m/z = 205 $[M+H]^+$.

^{1}H-NMR (400 MHz, chloroform-*d*) δ (ppm) = 5.76 (ddt, *J* = 16.1, 10.7, 5.6 Hz, 1H), 5.12 (d, *J* = 17.2 Hz, 1H), 5.02 (d, *J* = 10.3 Hz, 2H), 3.88 (d, *J* = 12.3 Hz, 2H), 3.51 (q, *J* = 6.1, 5.2 Hz, 12H), 3.22 (s, 3H).

^{13}C-NMR (101 MHz, chloroform-*d*) δ (ppm) = 134.57, 116.58, 71.87, 71.67, 70.35, 70.24, 69.17, 58.66.

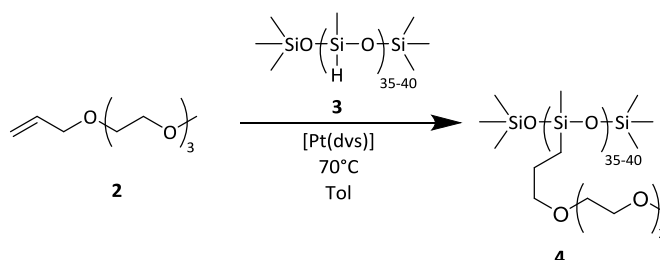Synthesis of polysiloxane-*comb*-propyl(triethylene oxide) **4** (PSx-PEO3)

Fig. S2: Reaction scheme of the synthesis of the polysiloxane-*comb*-propyl(triethylene oxide) 4 (PSx-PEO3).

The polysiloxane PSx-PEO3 **4** was synthesized via a hydrosilylation reaction according to KARATAS et al..[2] Triethylene glycol allyl methyl ether **2** was added to polymethylhydrosiloxane (PMHS) **3** under addition of the KARSTEDT-catalyst Pt(dvs). The product was obtained as clear and colorless viscous liquid.

^{1}H-NMR (200 MHz, toluene-d_8) δ (ppm) = 3.70-3.25 (OCH_2), 3.23-3.10 (OCH_3), 0.79-0.57 (Si-CH_2), 0.4-0.09 (Si-CH_3).

^{13}C-NMR (101 MHz, toluene-d_8) δ (ppm) = 104.59, 74.22, 74.16, 74.13, 73.10, 72.74, 72.46, 72.42, 72.34, 71.14, 71.11, 71.07, 71.00, 70.96, 70.84, 70.72, 70.68, 64.91, 62.29, 61.88, 58.72, 58.63, 26.78, 24.04, 14.25, 10.85, 9.18, 2.10, 0.10, -3.38.

<u>Preparation of membranes</u>

According to the literature[3], 2.5 g PVDF-HFP were dissolved in 50 g acetone (p.a.) at 50-60 °C under stirring. Then 4.5 g distilled water were added. The obtained homogenous solution was allowed to stand for 1 h at ambient temperature. Polymer solutions in various compositions (PVDF-HFP/PSx-PEO3 100/0; 90/10; 80/20; 70/30; 60/40; 50/50 in wt % based on the weight of PSx-PEO3/PVDF-HFP) were prepared. The solutions were stirred over night at room temperature and after further relaxing for 1 h the membranes were prepared by airbrush spraying. Therefore, the corresponding PVDF-HFP/PSx-PEO3-solution was sprayed on a Mylar®-foil or directly onto the electrode material with a *double action* spray gun with a full cone-type nozzle (HP-CR IWATA Revolution, N_2-stream, p = 2 bar) followed by evaporation of solvent under ambient conditions. The previously colorless solutions yielded in opaque membranes, which were subsequently dried in high vacuum (1 x 10^{-5} mbar) at 60 °C for at least 16 h.
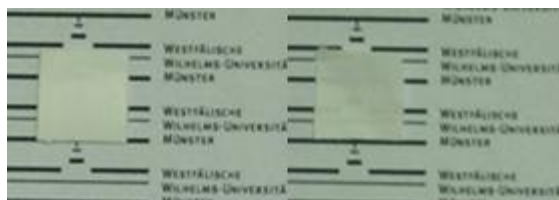

Fig. S3: Macroscopic pictures of a casted (left) and a sprayed (right) membrane.

<u>Applied materials and methods</u>

Gas chromatography linked with mass spectrometry (GC-MS)

The purity of the synthesized molecules was investigated by GC-MS measurements. The samples were analyzed by an ion trap mass spectrometer (Thermo Finnigan® GCQ*)* after separation by gas chromatography (column: SGE HT5 carborane-modified siloxane column).

Nuclear magnetic resonance spectroscopy (NMR)

For the NMR spectroscopic measurements a NMR spectrometer from *Bruker (Avance® III resp. Avance® I, 400 MHz)* was used. As solvents deuterized chloroform (99.8 atom% D, *Sigma Aldrich*), deuterized tetrahydrofurane (THF, 99.5 atom% D, *Euriso Top*) and deuterized toluene (99.5 atom% D, *Euriso Top*) were used. [1]H-, [13]C- and [29]Si-spectra were analyzed using the „MestReNova" software version 8.1.1-11591 (*Mestrelab Research S.L.®*).

Gel permeation chromatography (GPC)

GPC measurements provide information about the samples with respect to their molecular masses, their molecular mass distribution, their polydispersity and their viscosity. The synthetized polymers were examined with a gel permeation chromatograph Agilent 1100 (*Agilent Technologies®*). To avoid the irreversible adsorption of sample molecules to the column material, a 0.1 wt % solution of tetrabutylammonium bromide (TBAB) in THF was used as elution solvent. To prevent the formation of air bubbles a degasser (*DegasysPopulaire®*) was connected with the apparatus. Yielded polymers were dissolved in the elution solvent by obtaining sample solutions with concentrations of 4-6 mg mL^{-1}. The measurements were performed with a flow of 1.0 mL min^{-1} at a pressure of 50-60 mbar. By using an autosampler and an inlet valve (*Rheodyne®*), 50 µL of the investigated samples were initially transferred onto the type PSS-SDV precolumn (8-50 mm; *Polymer Standard Service GmbH*, modified styrol-divinylbenzene copolymer network). Afterwards, they were separated over two linear type PSS-SDV XL columns (8-300 mm, 5 µm, *Polymer Standard Service GmbH*). Finally, the samples were piped through two separated detectors, namely a refractometer (RI-detector, Agilent 1100) and a viscosimeter (η-1001, *WEG Dr. Bures®*). The obtained data was analyzed by the software „WINGPC Unity" version 6.20 (*Polymer Standard Service GmbH*). In this software the MARK-HOUWINK-equation (1) was considered and a statement about the molecular mass distribution of the investigated sample is possible.

$$\left[\eta\right] = K \cdot M^{\alpha} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity, M the molecular weight of the polymer and K and α the two constants, which are specific for a given polymer. By the analysis of the GPC elugrams a calculation average of the molecular weight M_w is possible.

Scanning electron microscopy (SEM) and SEM energy dispersive X-ray spectroscopy (EDX)

The membrane surfaces were investigated by scanning electron microscopy *(JEOL®, JSM-6510)* with a voltage of 5-15 kV. For an improved conductivity the membranes were previously sputtered with gold (20 s at 45 mA), to avoid charging effects.

For investigation of the elementary distribution of containing elements in the membranes SEM-EDX was used (20-25 kV).

SEM-EDX pictures were used to examine the homogeneity of the elemental distribution in the membranes. Regarding the pictures, airbrush spraying technique yield in membranes, with homogenously distributed polymers for all compositions (Fig. S4).
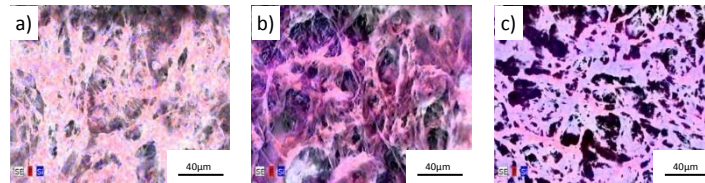

Fig. S4: SEM-EDX pictures of the surfaces of sprayed PVDF-HFP-membranes (a) 0 wt %, (b) 10 wt %, (c) 50 wt % PSx-PEO3. The observed elements are F (red) and Si (blue).

Differential scanning calorimetry (DSC)

For crystallinity analysis of the membranes with the different compositions (PVDF-HFP/PSx-PEO3) a differential scanning calorimeter (*Netzsch® DSC 204F1 Phoenix 240-12-00038-L*) was used. Samples were weighted into an aluminum pan and sealed. Subsequently, the temperature-depending heating curve of each sample in a temperature range from 20 °C to 250 °C (heating rate of 10 °C per minute) was plotted. During the measurement, each sample was heated three times and subsequently cooled down to obtain differences in curve shape, which imply morphological changes (Fig. S5). Determination of the molar melting enthalpy of the polymer electrolytes was implemented by considering each first curve. The integral under the peak correlates to the corresponding melting enthalpy. Subsequently, the crystallinity of the membranes could be calculated by using equation (2).

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \cdot 100\% \, , \qquad (2)$$

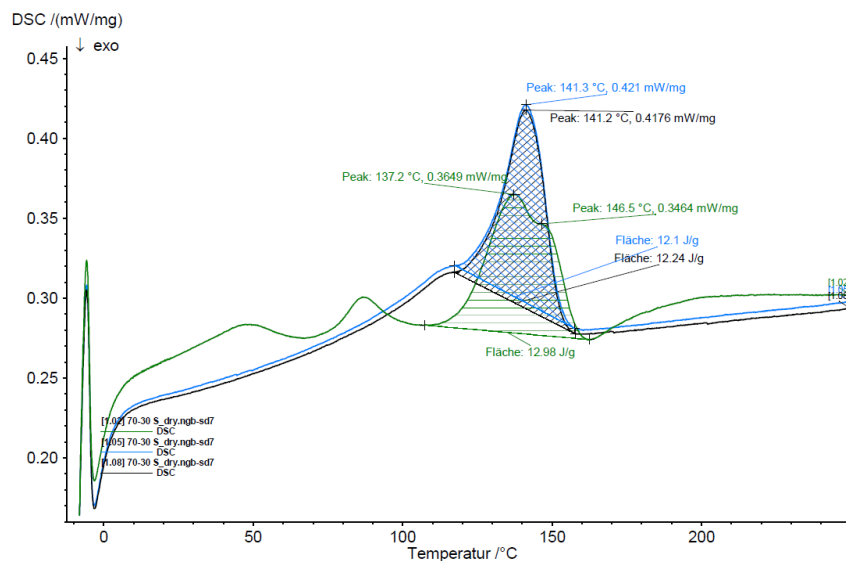where ΔH_m^0 is the standard melting enthalpy of crystalline PVDF (104.7 J g^{-1}).[4]

Fig. S5: Exemplary DSC-diagram for determination of ΔH_m.

Determination of the porosity

For the determination of porosities of the PVDF-HFP membranes a literature known process was applied, whereby the uptake of *n*-butanol was used. The membranes were immersed into *n*-butanol up to the complete absorption and they were weighed before and after the absorption. According to equation (3) the porosity was calculated.[4,5]

$$ P = \frac{(m_a - m_t) / \rho_{BuOH}}{\left(\dfrac{m_a - m_t}{\rho_{BuOH}} \right) + \dfrac{m_t}{\rho_t}} \cdot 100\% \, , \qquad (3) $$

where m_t is the weight of the dried membrane, m_a is the weight of the soaked membrane with *n*-butanol, ρ_t is the density of the dried membrane and ρ_{BuOH} the density of *n*-butanol.

Determination of the electrolyte uptake

The electrolyte uptake of the prepared PVDF-HFP membranes (E_{uptake}) was determined analogous to the determination of porosity by using equation (4).[4]

$$ E_{uptake} = \frac{m_a - m_t}{m_t} \cdot 100\% \, , \qquad (4) $$

where m_a is the weight of the membrane soaked with electrolyte and m_t is the weight of the dried membrane.

Electrochemical impedance spectroscopy (EIS)

The ionic conductivities were calculated using electrochemical impedance spectroscopy. The membranes were cut into 1 x 1 cm pieces, immersed into liquid electrolyte (EC/DMC 1:1, 1 M LiTFSI) till soaking saturation (roughly 1 – 2 min) and positioned between two ion blocking steel electrodes (d = 0.5 mm) into a measuring cell. During the measurement, the cell was fixed in the apparatus under inert gas conditions. The measuring apparatus was tempered in a temperature range of -20 °C to 60 °C by a thermostat (*Julabo® FP 45, Julabo Labortechnik GmbH*). A frequency analyzer (Agilent® E 4980 A) applied alternating voltage with an amplitude of 40 mV in the frequency range from 20 Hz to 2 MHz. The data was recorded with "ZPlot" and analyzed with the "ZView" software version 3.1c (*Scribner Ass, Inc.*).

The total ionic conductivity *σ* was calculated according to equation (7)

$$ \sigma = \frac{1}{R} \cdot \frac{d}{A} \, , \qquad (7) $$

where R is the measured resistance, d is the thickness of the sample and A the surface of the sample. The ratio of thickness and surface is usually referred to as the cell constant.

The ionic resistance of the prepared membrane systems was examined using impedance spectroscopy. Depending on the temperature the obtained impedance spectra were analyzed in two different ways. For high temperatures (20 °C to 60 °C), an inclined straight line was observed (Fig. S6). The values of R were received from the real-axis intercept. In this region the applied electrolyte shows almost only ohmic resistance.
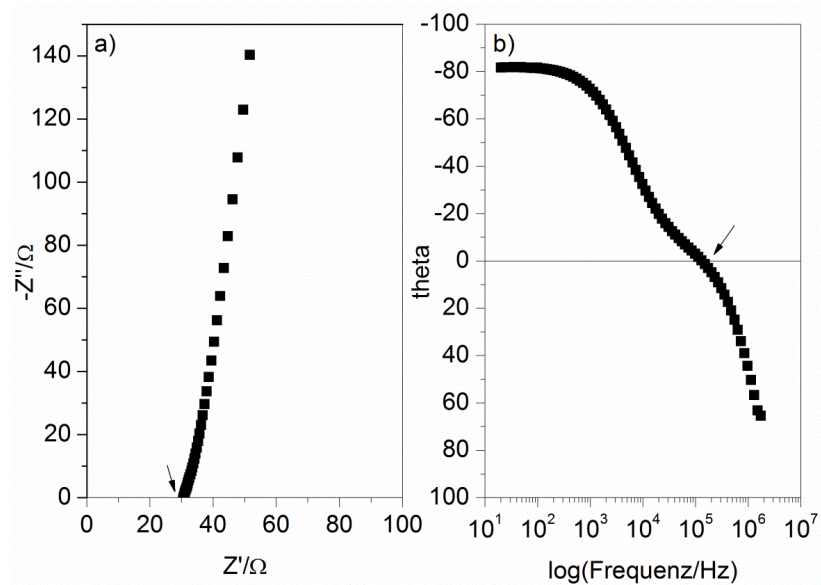

Fig. S6: Exemplary a) Niquist plot and b) Bode plot of a sprayed membrane with 20 wt % of PSx-PEO3 for high temperatures.

On the contrary, considering the obtained curve for low temperatures (-20 °C to 20 °C), some samples show a semi-circle (Fig. S7). In these cases an equivalent circuit diagram (ESB-1) had to be used to fit the data.[6]
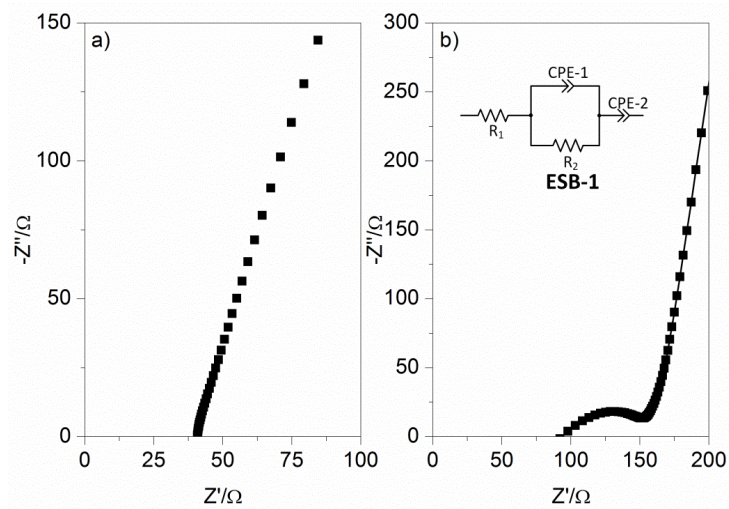

Fig. S7: Exemplary Niquist plot a) for high temperatures (20 °C to 60 °C) and b) low temperatures (-20 °C to 20 °C).

Preparation of Swagelok® T-cells

Electrochemical investigations (LSV and CCC) were carried out in lab-scale Swagelok® type T-cells with a three-electrode configuration using lithium metal as counter electrode (CE, Ø = 12 mm) and reference electrode (RE, Ø = 6 mm). The separator consisting of the PVDF-HFP PSxPEO3 80/20 membrane was directly sprayed onto the lithium iron phosphate (LFP) cathode, which was used as working electrode (WE, Ø = 12 mm). As electrolyte solution 1M LiTFSI in EC/DMC (1:1) or 0.7M LiBOB in EC/DMC (1:1) was used. The separators were soaked with 120 µL of electrolyte solution. Alternatively, the commercially available glass microfiber separator (Whatman GF/D) with 200 µL of the corresponding electrolyte solution was used instead of the airbrush sprayed membrane.

Linear sweep voltammetry (LSV)

In LSV measurements, the standard Swagelok® T-cells were connected to a potentiostat/galvanostat (Autolab PGSTAT302N, Deutsche Metrohm GmbH & Co. KG) in order to measure the electrochemical stability in the reductive and oxidative region. For the reductive measurement, Cu was used as WE with an operating potential range between -0.25 V and 2.25 V vs. Li/Li$^+$. The oxidative experiments were carried out using Pt as WE between 3.0 V and 7.0 V vs. Li/Li$^+$. In both cases Li metal was used as CE and as RE. The scan rate was appointed to 1.0 mV s^{-1} in all experiments. The data were recorded and analyzed with the software „NOVA" version1.10.4 (Metrohm Autolab B.V.) and „OriginPro" version 9.1 (OriginLab Corporation®).

Constant current cycling (CCC)

Constant current charge/discharge cycling was performed on a multichannel MACCOR S4000 battery test system (Maccor Inc.®). Two different experiments were conducted. On the one hand, the long-term cycling behavior was investigated applying five formation cycles with a current rate of 0.1C followed by the ongoing cycling at 0.5C. On the other hand, a C-rate test was realized applying current rates from 0.1C to 5C for 5 cycles each. In both cases, the lower and upper cut-off potential were set to 2.8 V and 4.0 V vs. Li/Li$^+$, respectively. The data was recorded and analyzed by the software „MACCOR" version MR 32-bit version 3.1.340 (Maccor Inc.® Tulsa, Ok, USA) and „OriginPro" version 9.1 (OriginLab Corporation®).
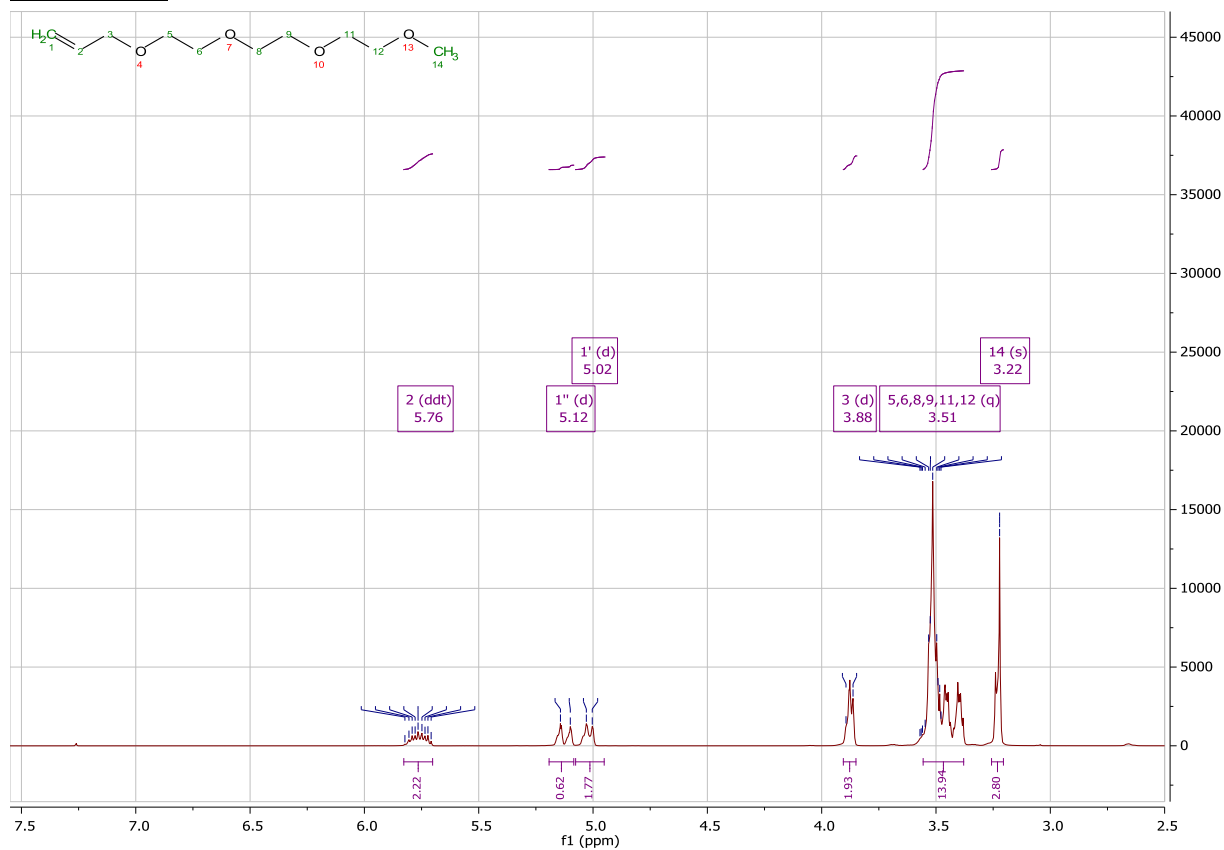
NMR spectra

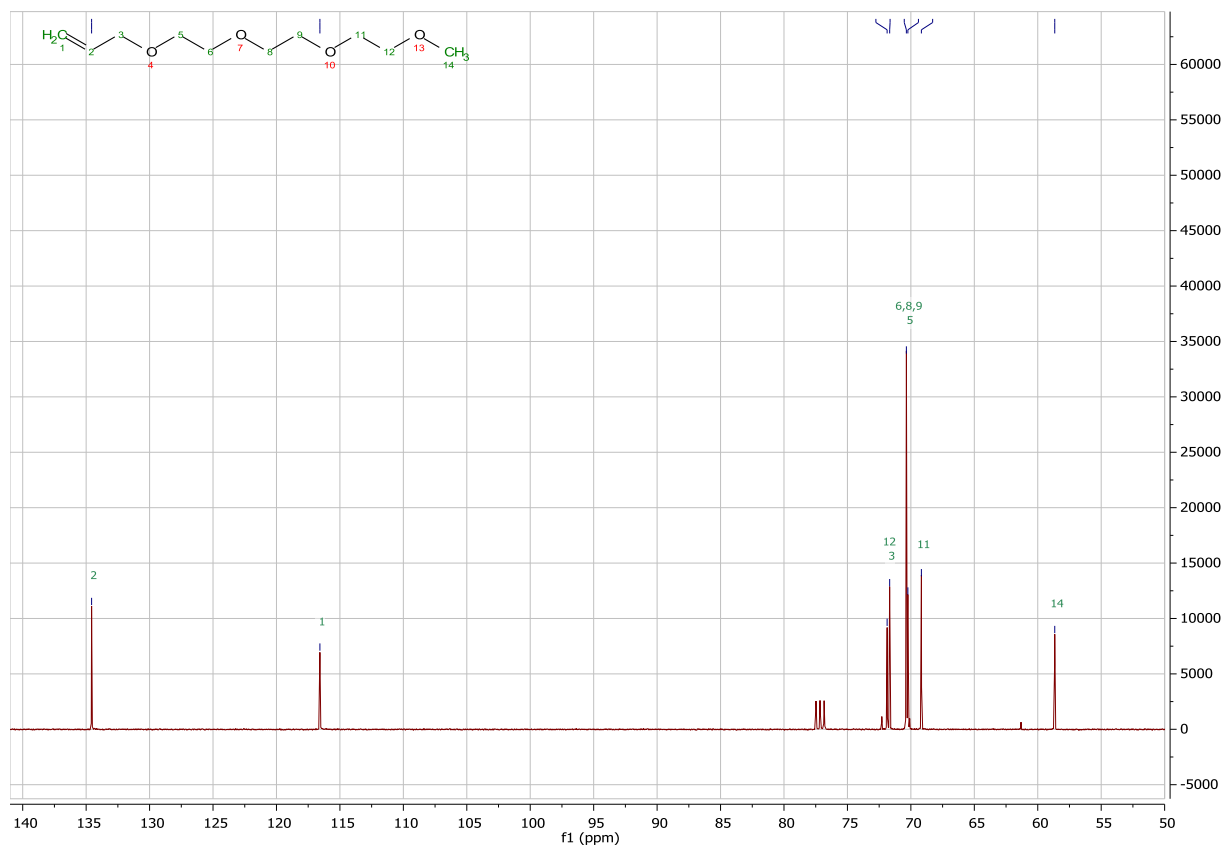Fig. S8: ^{1}H-NMR of the ethylene oxide functionality triethylene glycol allyl methyl ether 2 (PEO3).

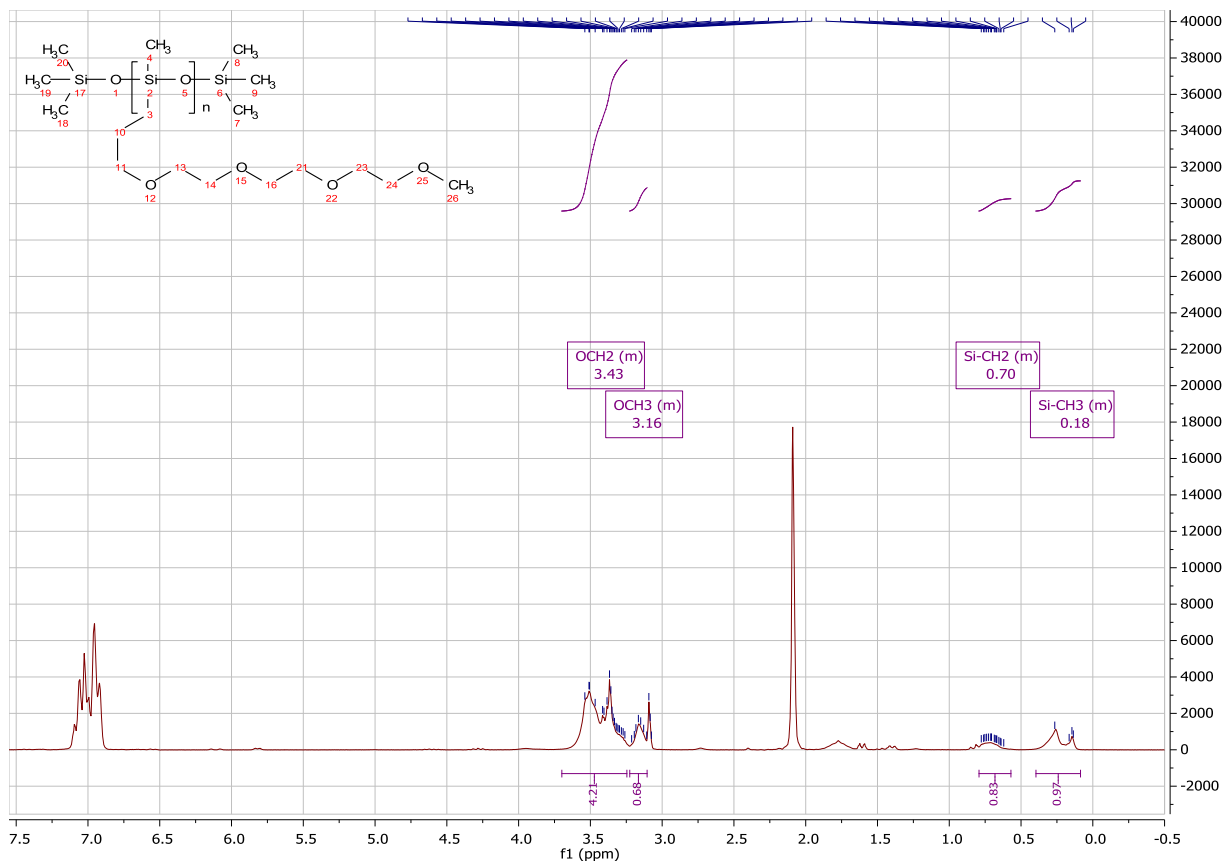Fig. S9: ^{13}C-NMR of the ethylene oxide functionality triethylene glycol allyl methyl ether 2 (PEO3).

Fig. S10: ^{1}H-NMR of the polysiloxane-*comb*-propyl(triethylene oxide) 4 (PSx-PEO3).

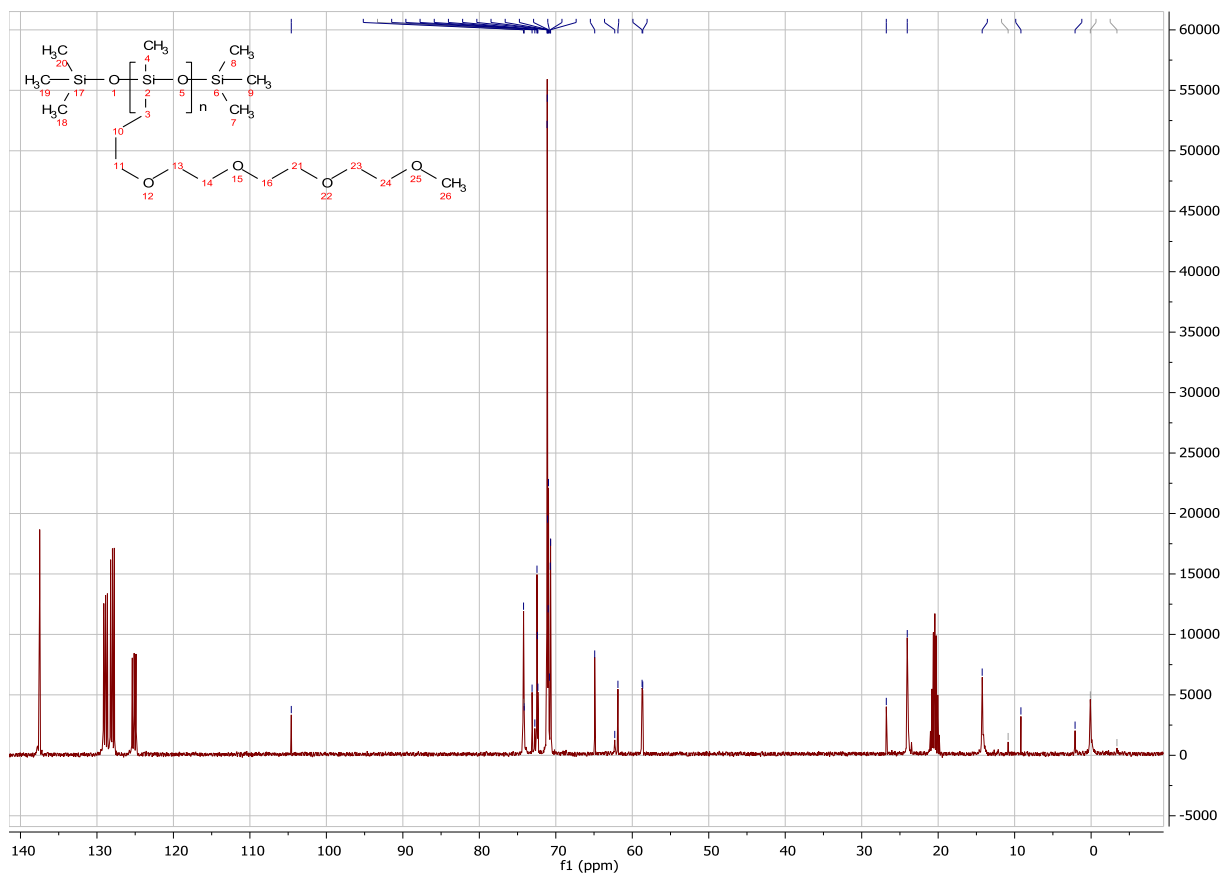OCH2 (m)
3.43

OCH3 (m)
3.16

Si-CH2 (m)
0.70

Si-CH3 (m)
0.18

Fig. S11: ^{13}C-NMR of the polysiloxane-*comb*-propyl(triethylene oxide) 4 (PSx-PEO3).

Tables

Tab. S1: Porosity, degree of crystallinity, electrolyte uptake and ionic conductivity at 20 °C of all sprayed membranes in dependence of the particular PSx-PEO3 amount.

Sprayed membranes	PSx-PEO3 amount/wt %					
	0	10	20	30	40	50
Porosity P/%	44	44	43	41	45	46
Crystallinity X_c/%	31.4	23.6	18.6	12.43	6.6	7.6
Electrolyte uptake E_{uptake}/%	517	479	520	423	404	322
Ionic conductivity σ(20 °C)/S cm^{-1}	4.12×10^{-5}	7.12×10^{-5}	4.22×10^{-4}	6.93×10^{-5}	2.28×10^{-4}	6.90×10^{-5}

References

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4. R. Prasanth, N. Shubha, H. H. Hng, and M. Srinivasan, *J. Power Sources*, 2014, **245**, 283–291.

5. Z. H. Li, C. Cheng, X. Y. Zhan, Y. P. Wu, and X. D. Zhou, *Electrochimica Acta*, 2009, **54**, 4403–4407.

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