A High-Performance Polysiloxane-Based Polymer Electrolyte for All-Solid-State Lithium Metal Batteries

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Experimental part

^{1}H and ^{13}C NMR spectra were recorded at 298K on a Bruker Avance 400NMR spectrometer using a 5 mm broadband inverse probe at 400.13 and 100.61 MHz, respectively. Chemical shifts (δ) in ppm were calibrated to residual solvent peaks (CDCl$_3$: δ = 7.26 and 77.16 ppm). Gel permeation chromatograms were recorded using an Agilent 1100 Series HPLC (Columns: serial coupled PSS SDV 5 m, 100Å and PSS SDV 5 m, 1000 Å, detector: DAD, 235 nm and 360 nm; refractive index), with THF as mobile phase. PDMS standards were used for calibration and toluene as an internal standard. Differential scanning calorimetry (DSC) investigations were undertaken on a Pyris Diamond DSC 8000 (Perkin Elmer USA) instrument under nitrogen flow (20 ml × min^{-1}), in aluminium crucibles shut with pierced lids and using about 15 mg sample mass. Thermal gravimetric analysis (TGA) was conducted on a Netzsch TG 209 F1 in Nitrogen (100% N$_2$).

The tensile tests were performed on a Zwick Z010 tensile test machine with a crosshead speed of 50 mm min^{-1} (278% min^{-1}). Tensile test specimens with a gauge width of 2 mm and a gauge length of 18 mm were prepared by die-cutting. The strain was determined using a longitudinal strain extensometer. The curves were averaged from 3 different samples. The elastic modulus Y was determined from the slope of the stress-strain curves using a linear fit to the data points within ±5% strain.

Permittivity measurements were performed in the frequency range from 10 Hz to 10^7 Hz using a Novocontrol Alpha-A frequency analyzer. The VRMS (root mean square voltage) of the probing AC electric signal applied to the samples was 1 V. The permittivity ε' was determined from the capacitance $C = \varepsilon'\varepsilon_0 A/d$, where A is the electrode area, d is the thickness of the film, and ε_0 is the vacuum permittivity. The thickness of the film was measured by a micrometer gauge with an uncertainty of ±5 μm. Two stainless steel discs with a diameter of 20 mm served as electrodes which were placed on the cross-linked film. Before measurement, the samples were dried in the vacuum oven.

Electrochemical studies were performed using CR2032 coin cells, assembled in an argon-filled glovebox (MBraun, O$_2$ and H$_2$O <0.1 ppm). For dielectric permittivity and conductivity measurements, two stainless steel blocking electrodes with a diameter of 16 mm and the polymer electrolyte films with a diameter of 16 mm and a thickness ~ 250 μm as electrolyte were used. Both properties were

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measured by using a Novocontrol broadband impedance spectrometer. For the conductivity, the electrochemical impedance spectroscopy (EIS) measurements were performed at 25 °C, 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C. The linear sweep voltammetry of the polymer electrolytes was measured by a Biologic VMP3 potentiostat with a lithium counter electrode with a diameter of 14 mm, a stainless steel working electrode with a diameter of 16 mm, and a scan rate of 0.1 mV s^{-1} between -0.2 V and 6 V at 60 °C.

Materials

Unless otherwise stated, all chemicals were reagent grade and used without purification. 2,2-Dimethoxy-2-phenylacetophenone (DMPA), 2,2'-(ethylenedioxy)diethanethiol (CL2), methanol, PEO (M_w = 1'000'000 g/mol), poly(vinylidene fluoride M_w = 600'000 g/mol), 2,2'-azobis(2-methylpropionitrile) (AIBN), tetramethylammonium hydroxide 25% in H_2O (TMAH), and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) were purchased from Sigma-Aldrich. 1,3,5,7-Tetramethyl-1,3,5,7-tetravinyl cyclotetrasiloxane was purchased from ABCR, lithium iron phosphate from MTI corporation, and carbon black (Super P) from MTI Corporation. Tetrahydrofuran (THF) was purchased from VWR. 2-Cyanoethylthiol and polymethylvinylsiloxane were prepared according to the literature.

Poly(3-ethylsulfanyl propionitrile methyl-co-methylvinyl)siloxane (PSi-S-CN) was prepared according to the literature.[1] Polymethylvinylsiloxane M_n = 91761 g/mol (30 g, 0.348 mol, 1 equiv.) was dissolved in distilled THF (900 mL) and mixed with DMPA (0.846 g, 0.009 equiv.) and 2-cyanoethylthiol (28.8 g, 0.331 mol, 0.95 equiv.). The mixture was degassed by using three freeze-pump-thaw cycles and then irradiated with a UVAHAND 25 GS H1 mercury vapour UV lamp from Hönle UV technology for 20 min. The resulted polymer was concentrated at a rotary evaporator and the residue was precipitated in methanol. The purification of PSi-S-CN was done by dissolution in THF and precipitation in methanol. This procedure was repeated four times. The polymer was stored and used as a 40 wt% solution in THF.
^{1}H NMR (400 MHz, CDCl$_3$, δ): 6.10 – 5.79 (m, 3H Si – C̲H̲ – C̲H̲$_2$), 2.85 – 2.78 (m, 2H, C̲H̲$_2$ – CH$_2$ – CN), 2.72 – 2.64 (m, 4H, C̲H̲$_2$ – S – CH$_2$ – C̲H̲$_2$ – CN), 0.97 – 0.89 (m, 2H, Si– C̲H̲$_2$ –), 0.18 (s, 3H, Si – C̲H̲$_3$);

Preparation of electrolyte elastomer by UV irradiation
PSi-S-CN (40 % solution in THF), 2,2'-(ethylenedioxy)diethanethiol, DMPA and various amount of LiTFSI (Table S1) were stirred for 4 h at RT. The formed solutions were kept overnight in the fridge (2 °C) to remove the bubbles. Thin films were prepared by doctor blade technique (blade thickness of 200 μm and 5 mm/s), the solvent was let to evaporate and then the films were cross-linked by UV light for 5 min. When the films were cross-linked immediately after the solution was coated, the films tend to rupture and to bend when detached from substrate. To overcome these, it was important to remove the solvent prior cross-linking. The cross-linked electrolyte films were dried in the vacuum oven overnight at 60 °C.

This procedure was used to make electrolytes used for the symmetric cells characterizations.

Preparation of electrolyte elastomer by heat (PSi-S-CN-10a)

To a solution of PSi-S-CN (40 %) (2.5 g) in THF, 2,2'-azobis(2-methylpropionitrile) (0.008 g) and different amounts of LiTFSI salt (Table S1) were added and stirred for 4 h at RT. Thin films were prepared by doctor blade technique (blade thickness of 200 μm and speed of 5 mm/s). The solvent was evaporated by keeping it in the vacuum oven at 50 °C for 24 h and the films were cross-linked at 110 °C for 24 h. The cross-linked electrolyte films were dried in the vacuum oven overnight at 60 °C prior use.

The thermally cross-linking of electrolyte was important for the manufacturing of the full battery, which allowed for a good contact with the cathode material.

Table S1. The composition of the polymer electrolytes

Sample	PSi-S-CN[a] [g]	PSi-S-CN [g]	LiTFSI [g]	CN:Li$^+$ molar ratio	cross-linker [μl]	DMPA [g]	AIBN [g]
PSi-S-CN0	2.5	1	0	-	50	0.005	-
PSi-S-CN5	2.5	1	0.32	5:1	50	0.005	-
PSi-S-CN10	2.5	1	0.16	10:1	50	0.005	-
PSi-S-CN10a	2.5	1	0.16	10:1	-	-	0.008
PSi-S-CN15	2.5	1	0.12	15:1	50	0.005	-
PSi-S-CN20	2.5	1	0.08	20:1	50	0.005	-

[a]A 40 wt% solution of PSi-S-CN in THF was used.

Preparation of PEO/LiTFSI electrolyte

PEO/LiTFSI electrolyte was prepared by mixing LiTFSI (0.33 g) and PEO (M_w = 1'000'000 g/mol) (0.5 g) in 10 ml acetonitrile. The resulting solution was then added into a Teflon well, dried in a hood overnight and then in a vacuum oven at 55 °C for 48 h. The resulting film had a thickness of ~160 μm.

Symmetric lithium cells

Symmetric lithium cells were assembled with two lithium-metal electrodes with a diameter of 12 mm and a thickness of 500 μm and a UV cross-linked polymer electrolyte film with a thickness ~ 250 μm in between. The symmetric lithium cells were cycled at 0.1 mA cm$^{-2|}$ for 1 h and 10 h lithium platting and stripping duration at 60 °C on a Biologic BCS-800 battery cycler.

Full lithium metal cells

Full lithium metal cells were assembled with the same 500 μm thick lithium and a thermally cross-linked PSi-S-CN-coated lithium iron phosphate cathode with areal capacity of 0.6 mAh cm^{-2}. The cathode slurry was comprised of 80 wt% lithium iron phosphate (MTI corporation), 10 wt% carbon black (Super P), and

10 wt% poly(vinylidene fluoride) (Sigma-Adrich) binder in a form of 5 wt% solution in NMP, and was mixed by Fritsch Mini-Mill Pulverisette 23 for 20 min. The slurry was then blade coated on a Al current collector with blade thickness of 250 µm, dried at room temperature for 6 h, and further dried in a vacuum oven at 110 °C for 12 h. Thereafter a solution of 40 wt% PSi-S-CN-10 in THF was coated on the cathode surface (blade thickness of 300 µm) and left for five minutes at RT to allow the electrolyte to fill the cathode's pores. When the cathode was saturated with electrolyte (about 5 min), another thin layer (blade thickness of 300 µm) of electrolyte mixture in THF was blade coated on the electrode surface and then dried in a hood overnight at 60 °C. The dried electrolyte was cross-linked at 110 °C for 48 h. The result PSi-S-CN coating has a thickness ~160 µm. The full cells were cycled at 0.1 mA cm^{-2} between 3.0 V and 3.9 V at 60 °C on a Biologic BCS-800 battery cycler.
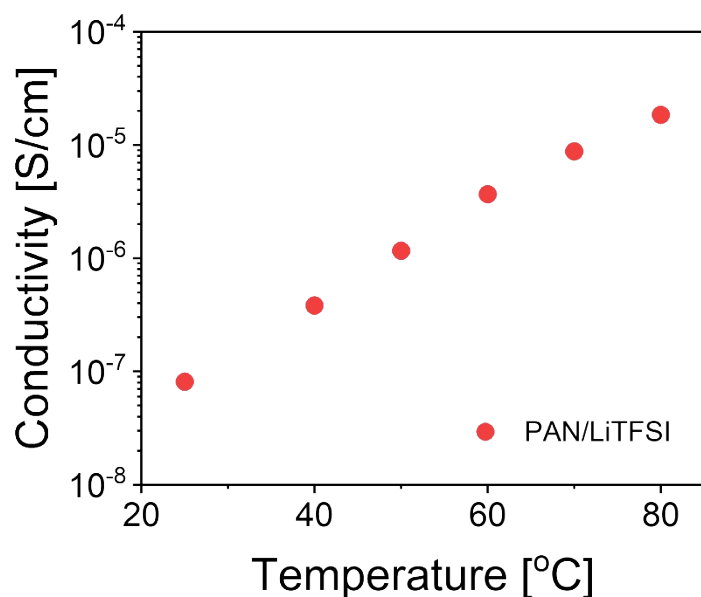
Fig. S1 Ionic conductivity of PAN/LiTFSI electrolyte.
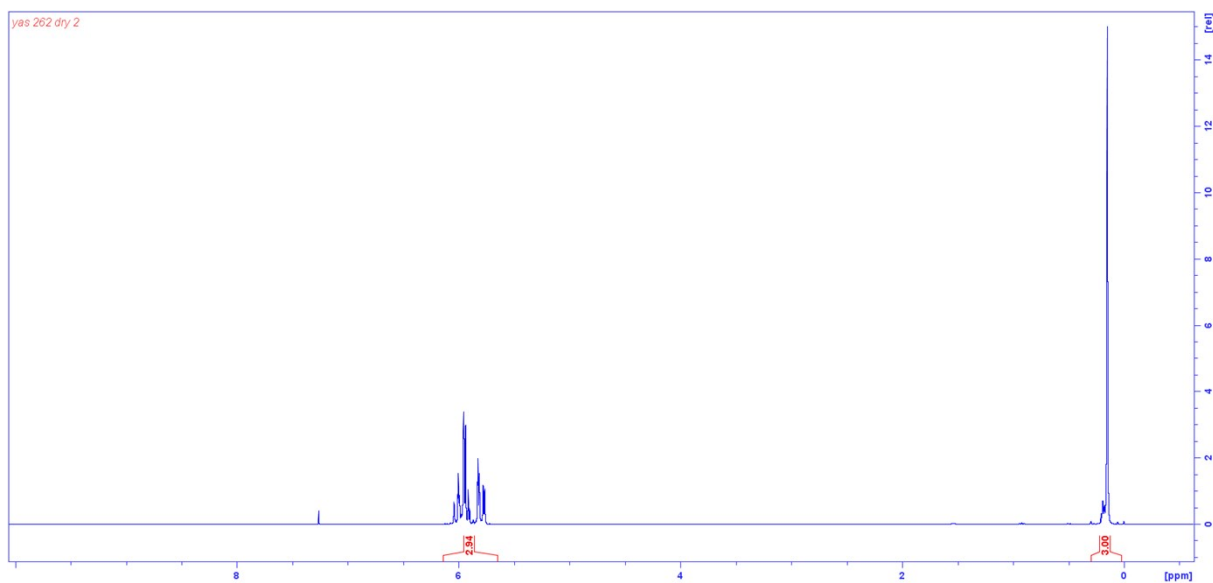
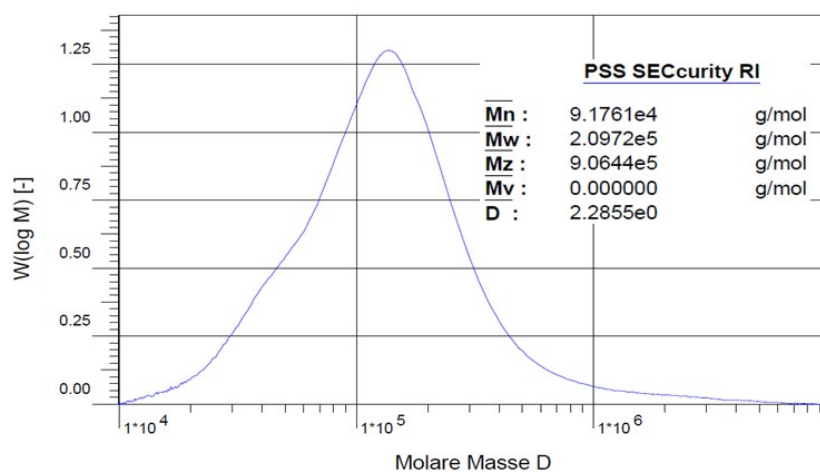**Fig. S2** ^{1}H NMR spectrum of polymethylvinylsiloxane.

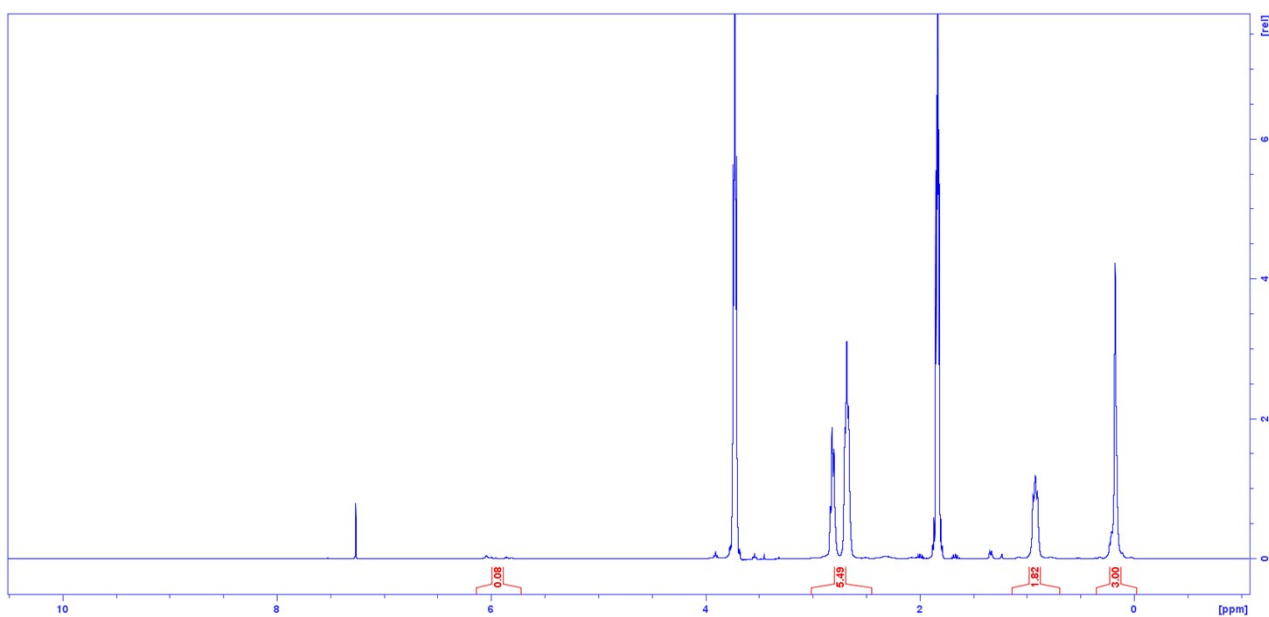**Fig. S3** GPC elution curve of polyvinylmethylsiloxane.

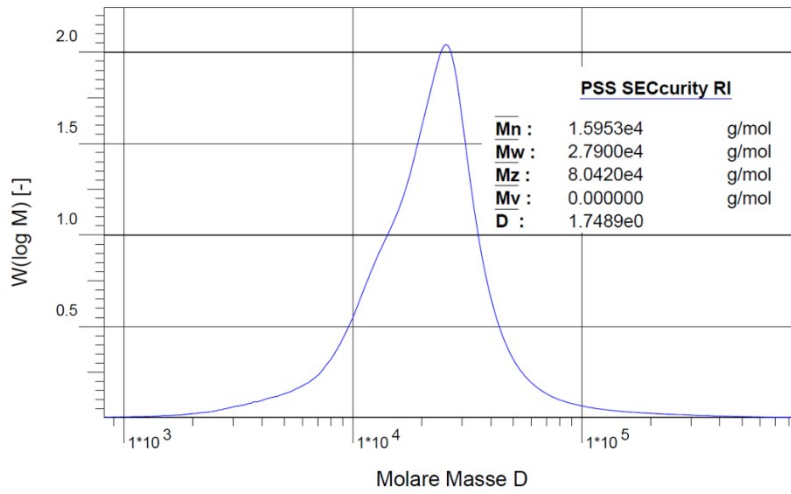**Fig. S4** ^{1}H NMR spectrum of PSi-S-CN.
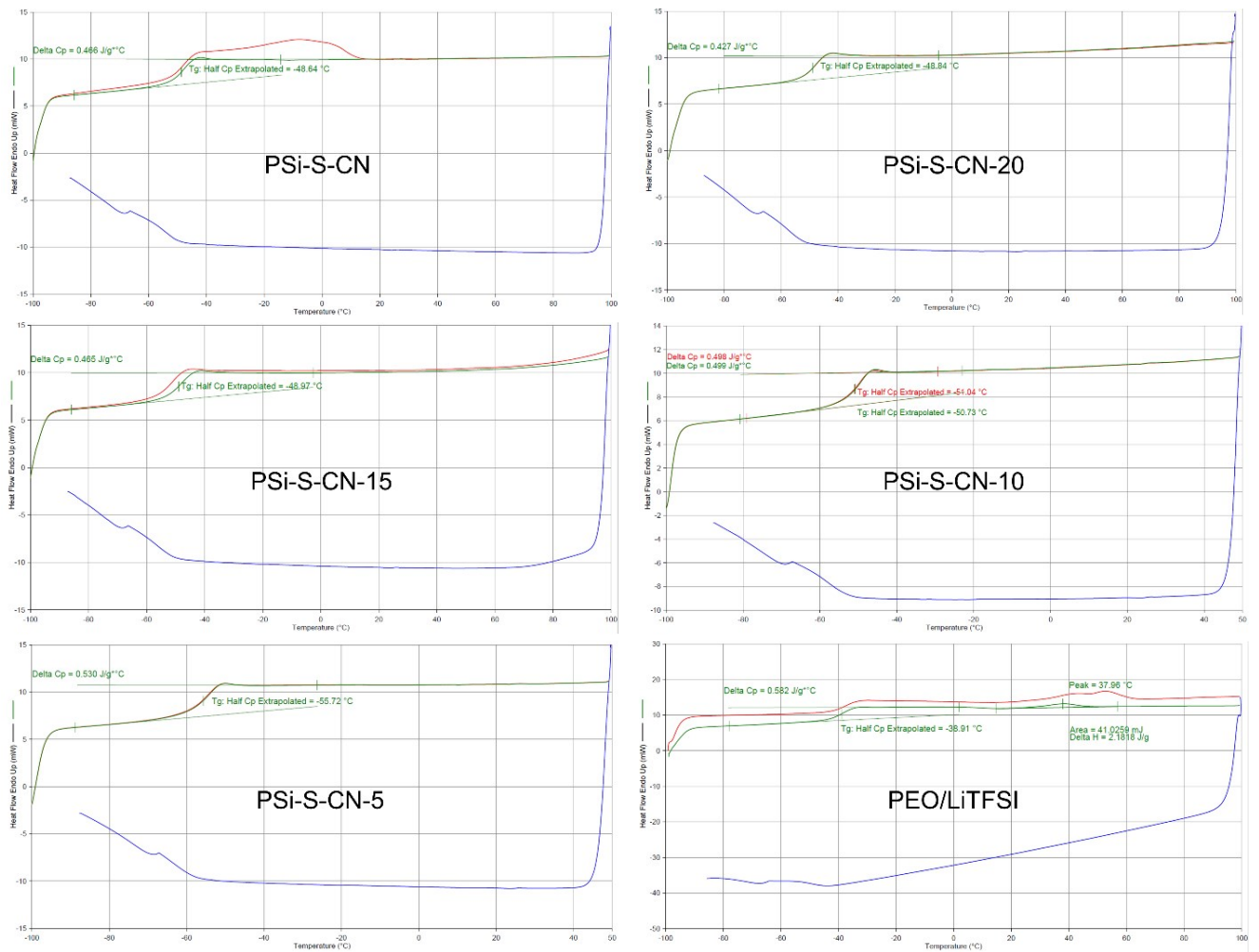
Fig. S5 GPC elution curve of PSi-S-CN.

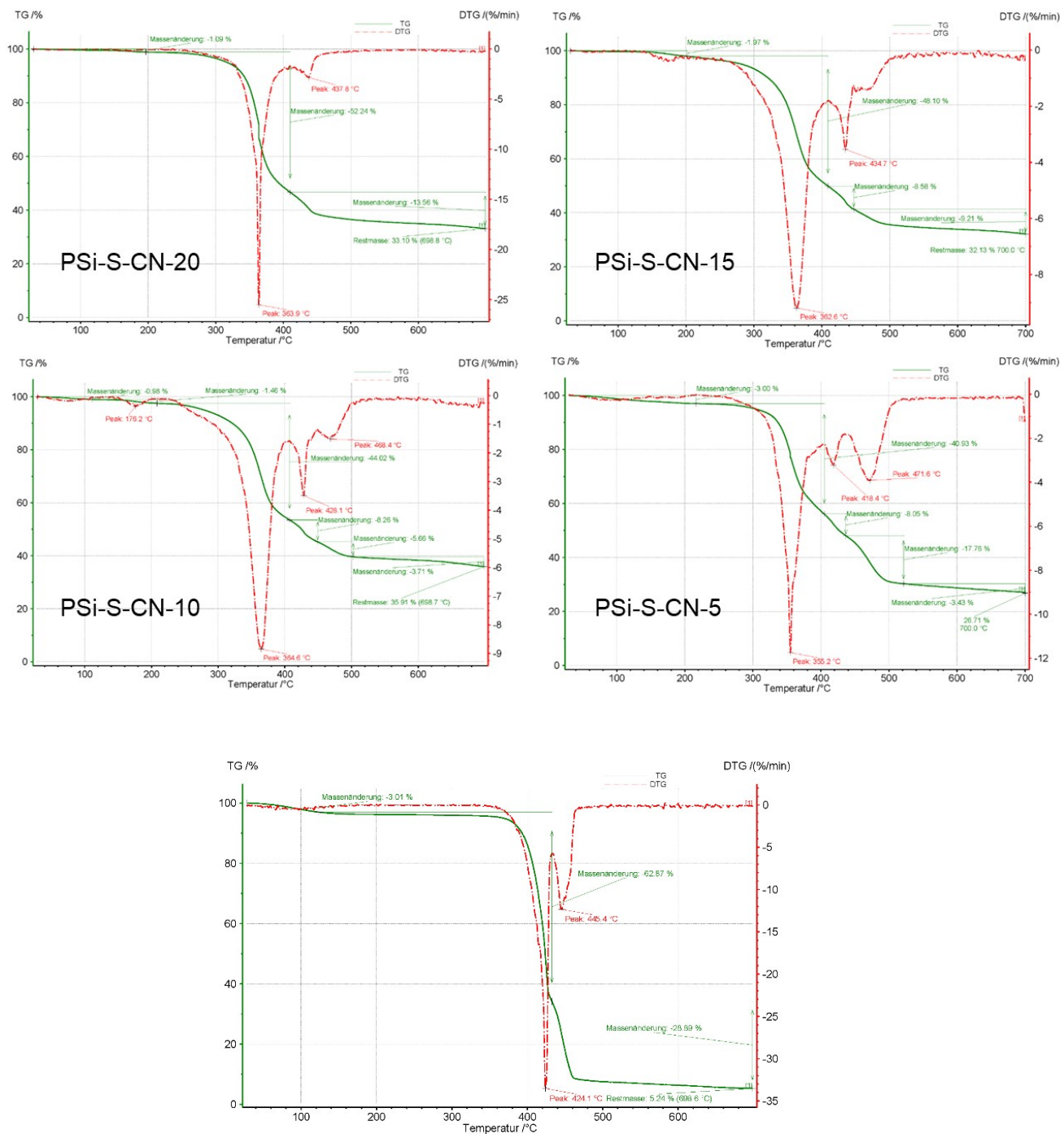**Fig. S6** DSC curves of different electrolytes.

Fig. S7 TGA curves of different electrolytes PSi-S-CN-X and of PEO electrolyte. The first decomposition peak is due to the polymer while the second is likely due to the Li salt used.
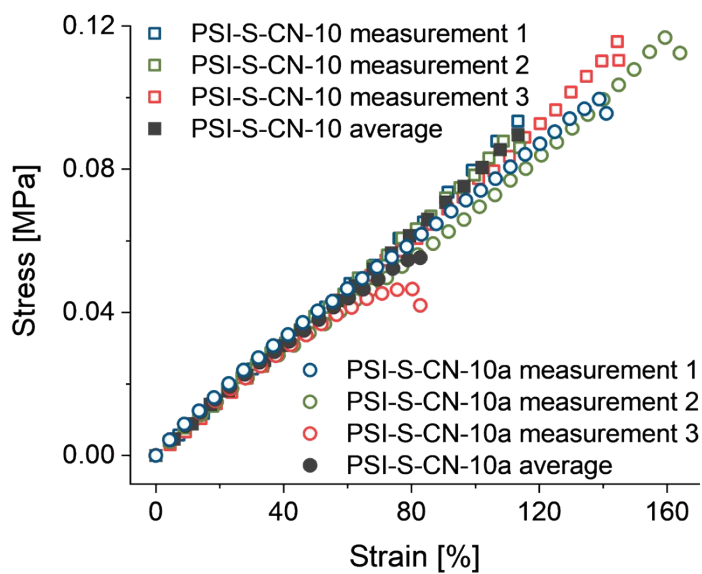
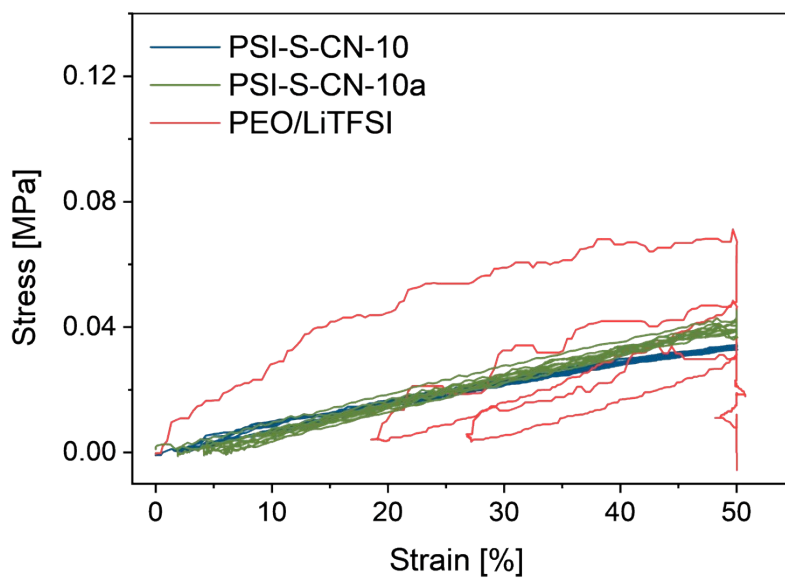**Fig. S8** Stress-strain curves of PSi-S-CN-10.

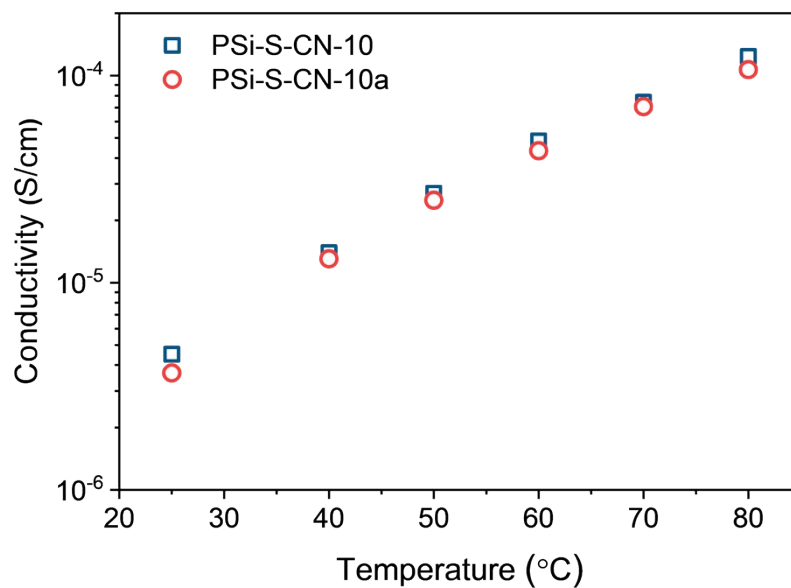**Fig. S9** Cyclic uniaxial tensile tests at 50 % strain for 5 cycles at RT.

Fig. S10 Ionic conductivity at different temperatures for PSi-S-CN-10 UV cross-linked and PSi-S-CN-10a thermally cross-linked electrolyte.
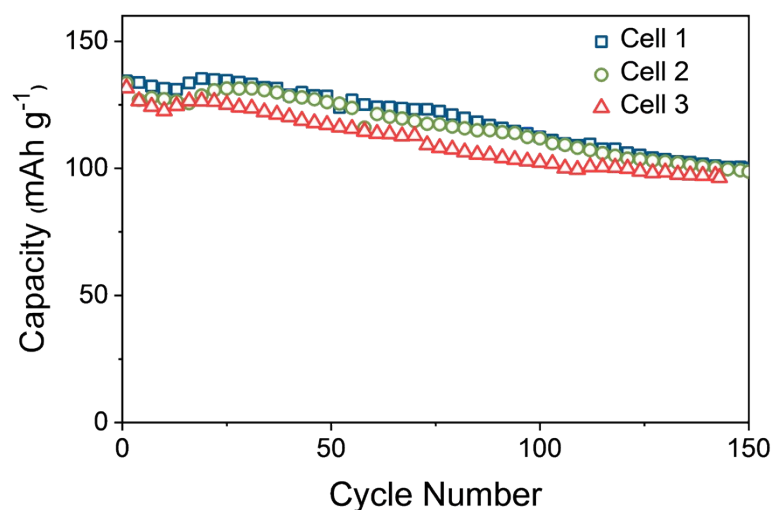

Fig. S11 Galvanostatic cycling of the all-solid-state full cells with 0.6 mAh cm^{-2} LFP cathode and lithium metal anode at 0.1 mA cm^{-2} at 60 °C. All three cells showed consistent cycle stability.

Table S2. Ionic conductivity at different temperature of electrolytes PSi-S-CN-10 UV and PSi-S-CN-10a thermally cross-linked, respectively.

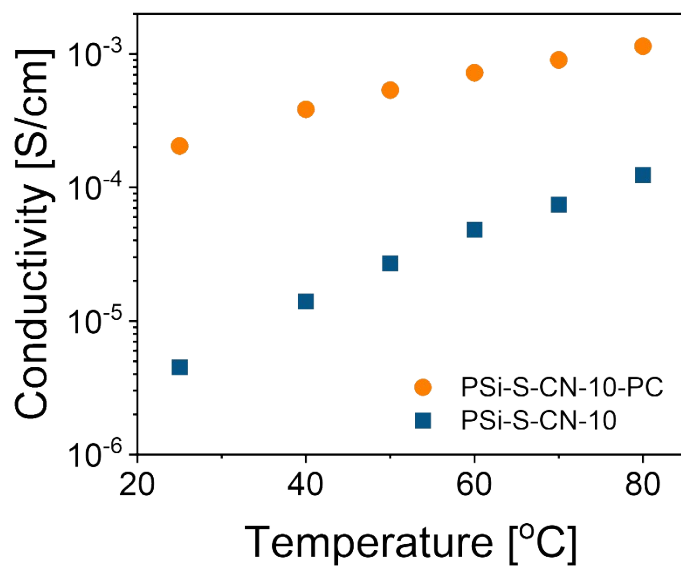| T [°C]	σ of PSi-S-CN-10 UV cross-linked [S/cm]	σ of PSi-S-CN-10a thermally cross-linked [S/cm]
25	4.51×10^{-6}	3.66×10^{-6}
40	1.40×10^{-5}	1.30×10^{-5}
50	2.70×10^{-5}	2.50×10^{-5}
60	4.83×10^{-5}	4.33×10^{-5}
70	7.43×10^{-5}	7.07×10^{-5}
80	1.24×10^{-4}	1.07×10^{-4}

Fig. S12 Ionic conductivity of PSi-S-CN-10 soaked in 1 M LiTFSI in propylene carbonate for 30 s.

Reference

1   Y. Sheima, P. Caspari and D. M. Opris, *Macromol. Rapid Commun.*, 2019, **40**, 1.