Westfälische Wilhelms-Universität Münster

Characterization of *semi*-interpenetrating Polymer Electrolytes containing PVDF-HFP and Ether-modified Polysiloxane for LIB Application

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Introduction

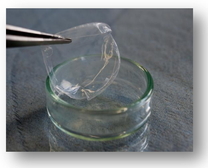
Semi-interpenetrating polymer networks (sIPN) merge the properties of their constituting ingredients to form solid polymer electrolytes (SPEs) for thin-film application in lithium-ion batteries:

Polysiloxane

- Highly flexible Si–O-bonds in backbone, low glass transition temperature,
- versatile chemical modification possibilities; e.g. ether functionalities for ion transport.

Poly(vinyl fluoride-hexafluoropropylene) (PVDF-HFP)

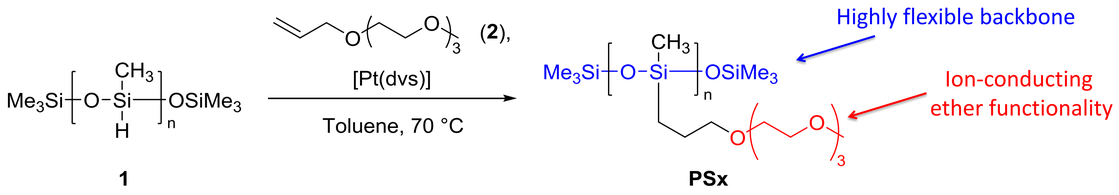
- Commercially available *co*-polymer,
- *Semi*-crystalline, thermoplastic, dielectric properties,
- Valuable for membrane preparation (e.g. ultrafiltration).



(*net*-PVDF-HFP)-*sipn*-PSx

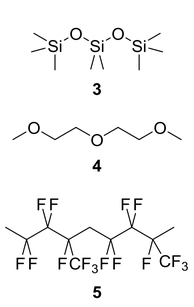
- ✓ Free-standing membrane,
- ✓ Fast & Easy-to-prepare,
- ✓ Ion-conducting,
- ✓ < 10 µm thickness viable.

Synthesis of Ether-modified PSx



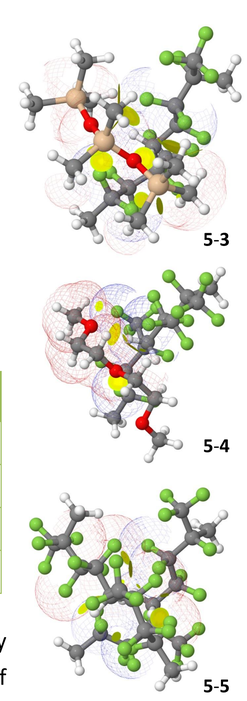
Reactions proceeded efficiently leading to formation of polysiloxane-*comb*-propyloxymethoxytriglycol **PSx**.

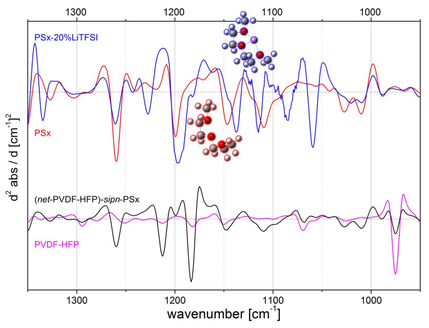
Computational Investigation



Simplified small molecules **3** - **5** to imitate domains of different polarity in *semi*-IPN:

- Geometries pre-optimized with MM3 force-field, DFT-optimized with B97D/6-311G(d,p) in gas phase.
- Computation of pairings **5**-X (X = **3** - **5**) to clarify interactions between present domains.
- Comparing interaction-induced frequency shifts from experimental and computational set up.



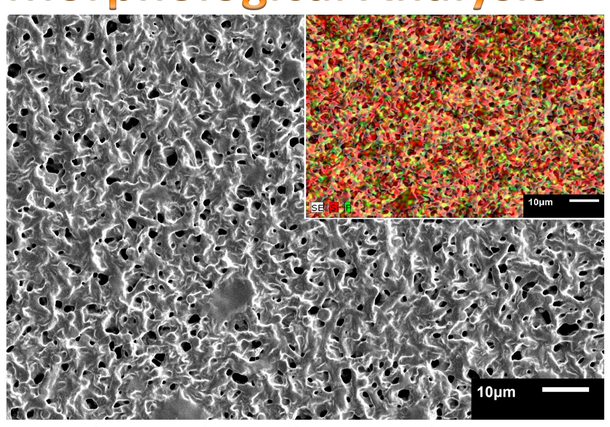


2nd derivative FTIR spectra to identify interaction-induced frequency shifts in (*net*-PVDF-HFP)-*sipn*-PSx electrolytes.

δ [in MPa½], ΔG [kcal mol⁻¹].			
Polymer (X)	δ	R_a	ΔG^{5-X}_{BSSE}
PDMS (**3**)	16.6	13.1	9.4
PEO (**4**)	20.3	4.1	6.3
PVDF-HFP (**5**)	22.8	-	5.9

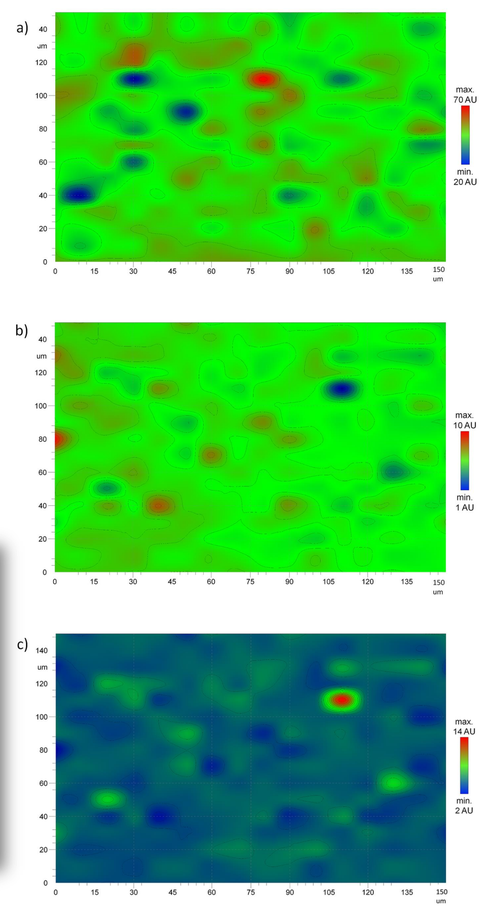
Amphiphilic properties of PSx proven by qualitative results of GIBBS free energy of formation ΔG^{5-X} and HANSEN total solubility parameter δ and distance R_a.

Morphological Analysis



SEM and SEM-EDX images of porous membranes.

- Porous (*net*-PVDF-HFP)-*sipn*-PSx membrane prepared by solution casting technique
  - Porosity Φ = 26 %, degree of crystallinity X_c = 10 %.
- X_c decreases with increasing amounts of PSx indicating that the formation of the PVDF-HFP α-phase is inhibited by PSx.
- Homogeneous distribution of PSx across (*net*-PVDF-HFP)-*sipn*-PSx membranes.
- Addition of PSx to PVDF-HFP matrix results in a noticeable change in tensile strain and stress.

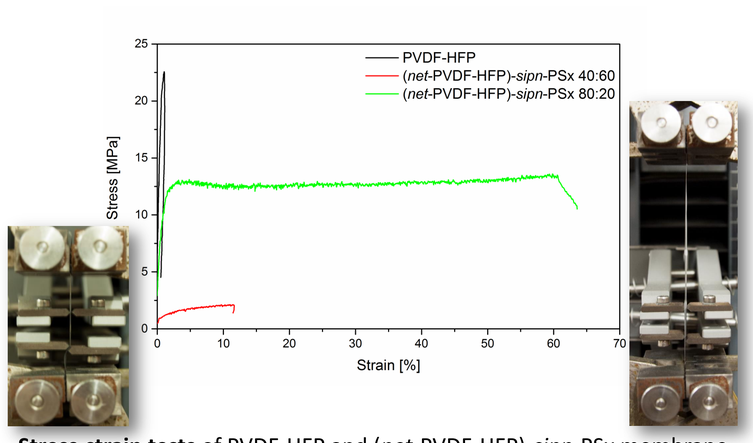


FTIR microscope mapping of (*net*-PVDF-HFP)-*sipn*-PSx membrane.

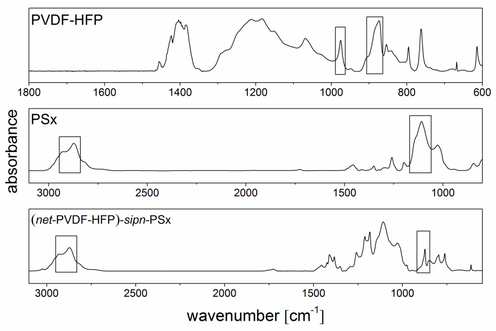
a) Chemical mapping of PVDF-HFP (sum of α-phase ũ = 980-970 and β-phase 890-865 cm^{-1}).
b) Chemical mapping of PSx (sum of C–H stretching ũ = 2950-2750 and O–CH_3 stretching 1150-1070 cm^{-1}).
c) Map of the ratio of integrated areas between ũ = 2950-2750 and 890-865 cm^{-1}.

AU: arbitrary absorbance unit.

DSC data of *semi*-IPN with melting point ($T_{m\text{-}PVDF\text{-}HFP}$), glass transition temperature ($T_{g\text{-}PSx}$), heat of fusion (ΔH_m) and the degree of crystallinity (X_c).						
PVDF-HFP [wt.%]	PSx [wt.%]	LiTFSI [wt.%]	$T_{g\text{-}PSx}$ [°C]	$T_{m\text{-}PVDF\text{-}HFP}$ [°C]	ΔH_m [J g^{-1}]	X_c [%]
Variation of (*net*-PVDF-HFP)-*sipn*-PSx						
100	0		-	133	24.6	24
0	100		-94	-	-	-
50	50		-85	132	17.3	17
40	60		-86	134	10.8	10
30	70		-85	131	8.1	8
Variation of LiTFSI in *semi*-IPNs						
38	57	5	-78	130	7.3	7
36	54	10	-64	130	6.6	6
34	51	15	-55	125	7.1	7
32	48	20	-43	125	7.1	7
30	45	25	-40	125	7.1	7

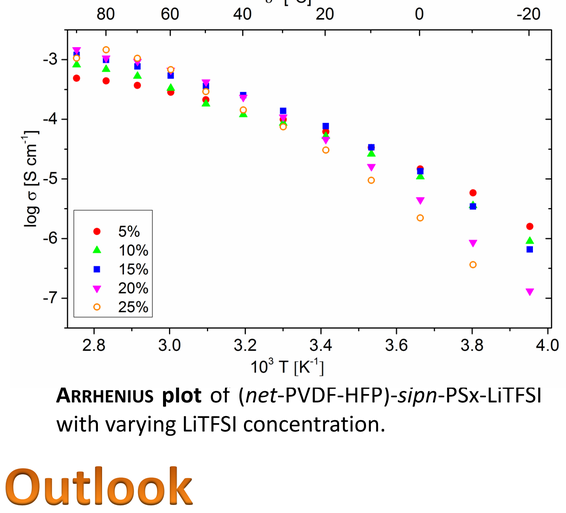


Stress-strain tests of PVDF-HFP and (*net*-PVDF-HFP)-*sipn*-PSx membrane.



FTIR spectra of pure PVDF-HFP, PSx and a (*net*-PVDF-HFP)-*sipn*-PSx network with integrals (black frames) used for FTIR mapping.

Electrochemical Analysis



ARRHENIUS plot of (*net*-PVDF-HFP)-*sipn*-PSx-LiTFSI with varying LiTFSI concentration.

$$\sigma_{eff.} = \frac{\sigma_0 \cdot \varepsilon}{\tau} = \frac{\sigma_0 \cdot \varepsilon}{(N_M \cdot \phi)} = \frac{\sigma_0 \cdot \varepsilon}{(\frac{\sigma_0}{\sigma_{sIPN}} \cdot \phi)}$$

Interpretation of ion transport

$\sigma_{eff.}$	effective conductivity
N_M	MACMULLIN-number
Φ	porosity
τ	totuosity
σ_0	conductivity PSx-LiTFSI
σ_{sIPN}	conductivity *semi*-IPN
ε	volume fraction

Properties of *semi*-IPN electrolyte membrane with LiTFSI.				
	semi-IPN-10	*semi*-IPN-15	*semi*-IPN-20	*semi*-IPN-25
N_M	1.6	1.6	1.3	8.2
Φ	0.45	0.45	0.45	0.45
τ	1.16	0.72	0.94	0.58
σ_0 [S cm^{-1}]	1.3×10^{-4}	1.2×10^{-4}	4.0×10^{-5}	2.5×10^{-5}
σ_{sIPN} [S cm^{-1}]	5.2×10^{-5}	7.7×10^{-5}	4.7×10^{-5}	3.0×10^{-5}
$\sigma_{eff.}$ [S cm^{-1}]	7.5×10^{-5}	1.1×10^{-4}	6.6×10^{-5}	4.4×10^{-5}

- Calculation of $\sigma_{eff.}$ to distinguish the effective contribution of PSx and PVDF-HFP to the overall ionic transport.
- Calculated tortuosity values τ<1 consider an explicit or implicit contribution of PVDF-HFP on ion transport.
- Since no PVDF-HFP/Li^+ interactions are observed from FTIR, an implicit contribution of PVDF-HFP is implied, e.g. by improving salt dissociation due to its high dielectric constant of 11.4.

Outlook

a) Modification of polysiloxane
- for higher Li^+ ion mobility.
- to increase miscibility between PVDF-HFP and polysiloxane.

b) Modification of host matrix
- Crosslinking of host matrix and polysiloxane.

c) Electrochemical measurements
- Cycling performance tests.
- C-rate tests.

References

- Cznotka, E.; Jeschke, S.; Vettikuzha, P.; Wiemhöfer, H.-D. *Solid State Ion.* **2015**, *274*, 55–63.
- Cznotka, E.; Jeschke, S.; Wiemhöfer, H.-D. *J. Membr. Sci.* **2015**, submitted.

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