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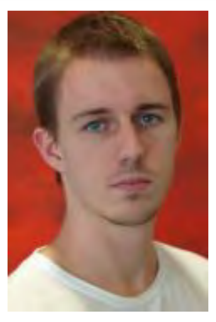

In cooperation with Leica Microsystems

Modified Siloxanes as Electrolytes for Application in Lithium-Ion Batteries

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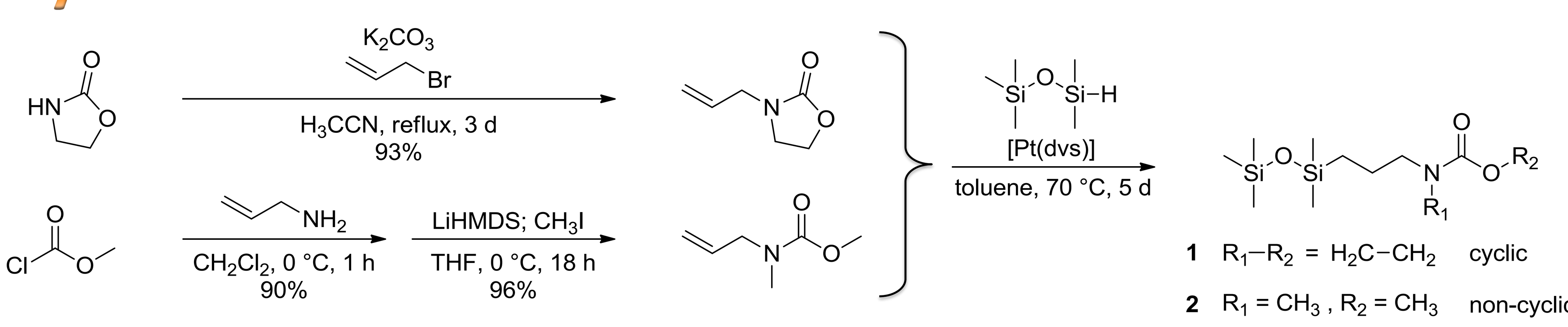
Introduction

Siloxanes desired due to their:

- low linearization energy (1.3 kJ/mol) and low rotation barrier (2.5 kJ/mol) of Si–O-bonds in backbone,
- low glass transition temperatures and non-toxicity,
- easy accessibility as starting materials; mostly industrial by-products,
- versatile chemical modification possibilities; e.g. preparation of free-standing solid polymer electrolytes, liquid additives and electrolytes, ionic liquids.

Synthesis of Carbamate-modified Disiloxanes

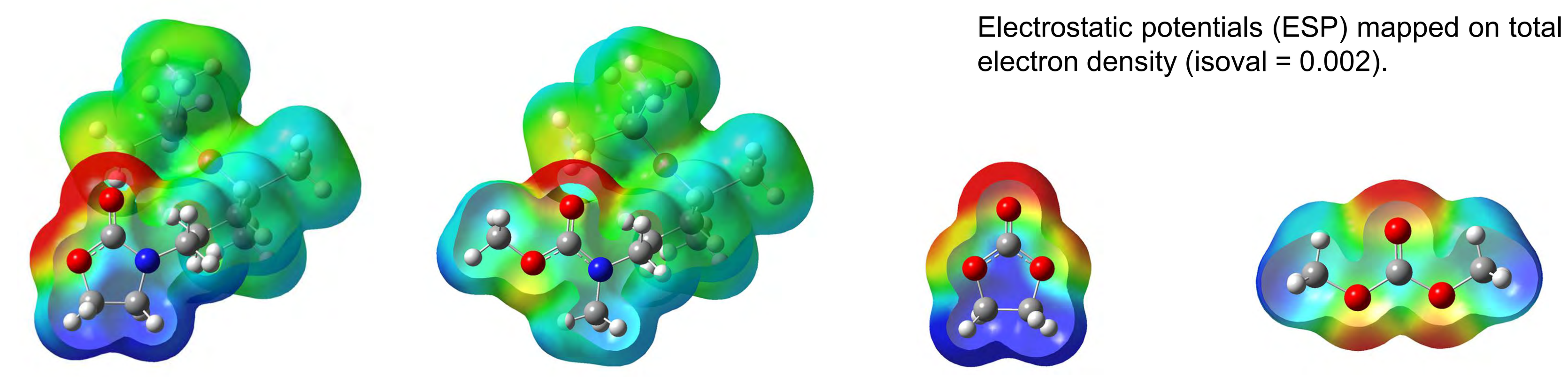


Electrochemical Characterization

Electrochemical potentials *vs.* Li/Li+ and calculated HOMO/LUMO values according to MOPAC2009.	1	2
Oxidation potential/V	4.5	4.8
Reduction potential/V	0	0
HOMO/eV	-9.5	-9.3
LUMO/eV	0.9	1.0

Ionic conductivities for electrolyte solutions of 1 with LiTFSI.	L-5	L-10	L-15
Content of LiTFSI/wt %	5	10	15
Conductivity σ (90 °C)/S cm^{-1}	1.4×10^{-3}	1.0×10^{-3}	1.2×10^{-3}
Conductivity σ (20 °C)/S cm^{-1}	2.7×10^{-4}	1.6×10^{-4}	1.4×10^{-4}
Conductivity σ (-20 °C)/S cm^{-1}	2.5×10^{-5}	1.1×10^{-5}	6.3×10^{-6}

Computational Approach



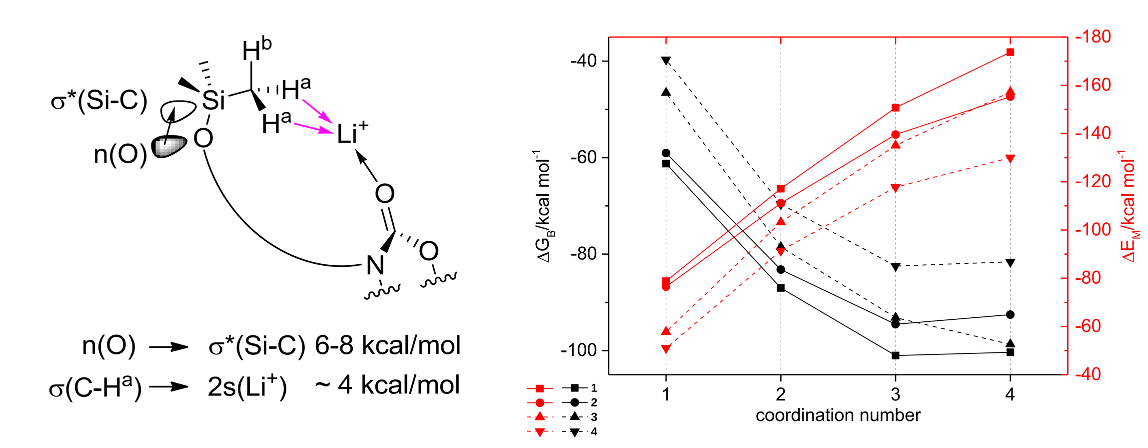
Electrostatic potentials (ESP) mapped on total electron density (isoval = 0.002).

1	2	ethylene carbonate (EC, 3)	dimethyl carbonate (DMC, 4)
ESP_{max} = -0.0789	ESP_{max} = -0.0695	ESP_{max} = -0.0685	ESP_{max} = -0.0594
μ_{calc} = 4.76 D	μ_{calc} = 2.14 D	μ_{calc} = 5.34 D	μ_{calc} = 0.30 D
ε_r = 28	ε_r = 7	ε_r = 90	ε_r = 3

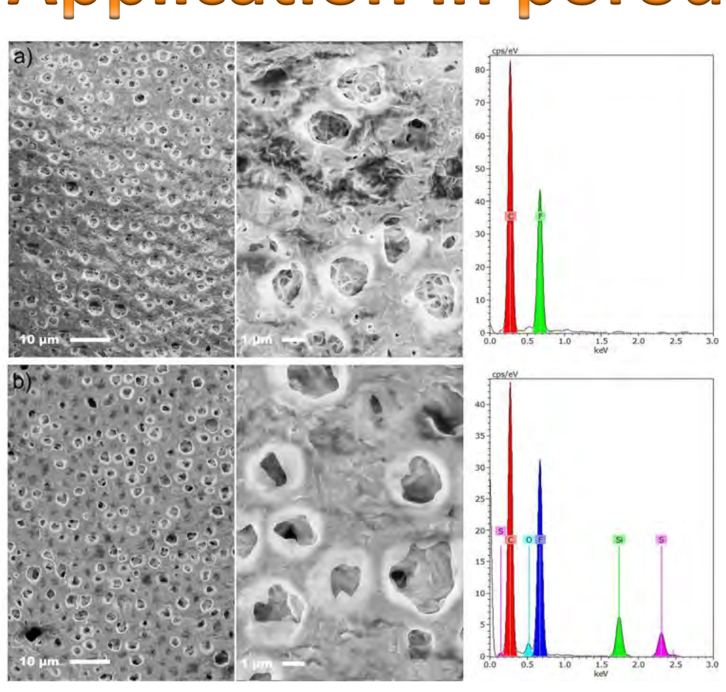
- Geometries optimized at B3LYP/6-311G(d,p) level of theory.
- Gibbs Free energies of solvation ΔG_B and solvent-solute interactions ΔE_M of solvation structures $[Li(\mathbf{S})_{n=1-4}]^+$ (S = **1** - **4**) computed.
- Natural bond order analysis: n(O)→σ*(Si–C) hyperconjugation in Si–O-bond favors $SiCH_2$–H···Li^+ interactions.

Donor-Properties Outrun Electrostatic Interactions

Important for the Development of Novel Solid Polymer Electrolytes



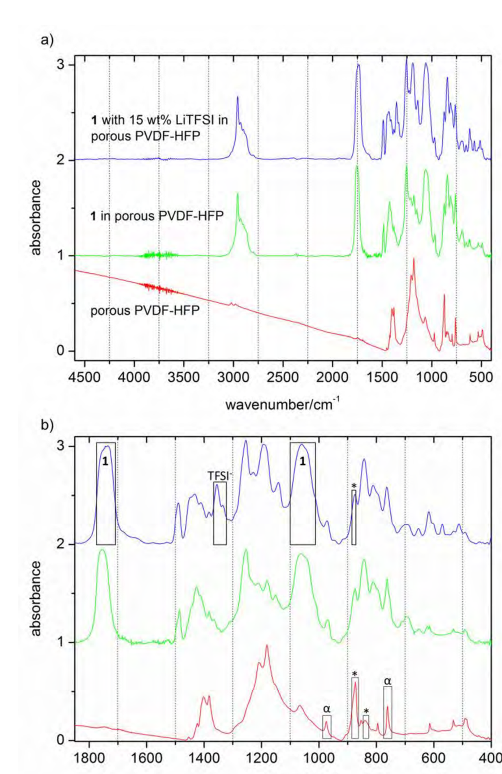
Application in porous PVDF-HFP Frameworks



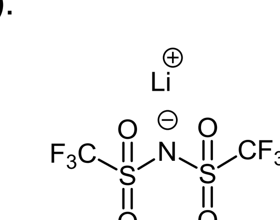
SEM images and corresponding EDX spectra of the porous membranes.
a) dry PVDF-HFP framework.
b) gel electrolyte membrane **M-5**.

- Porous PVDF-HFP membrane prepared by phase inversion (acetone/water).
  - degree of crystallinity X_c=36 %; porosity ϕ=51%.
- Activated gel electrolyte membranes M-X by soaking them in corresponding electrolyte solutions of **1** L-X (X=5, 10, 15 wt % of LiTFSI).

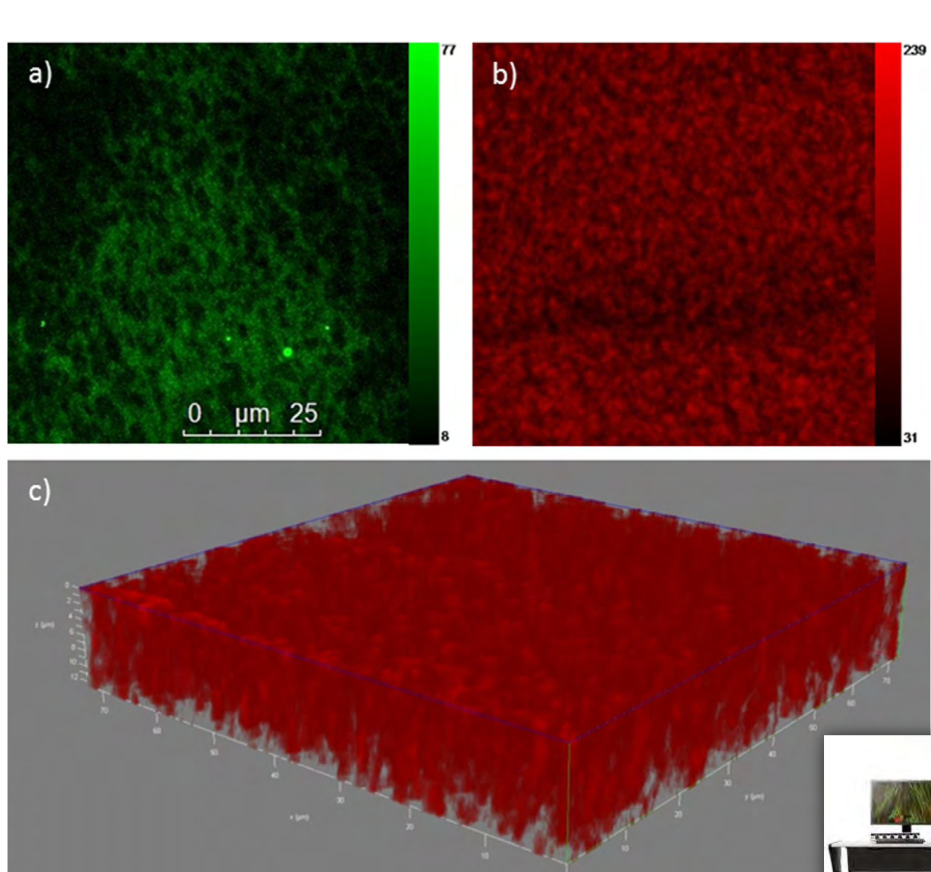
Properties of PVDF-HFP gel electrolyte membranes.	M-5	M-10	M-15
Thickness dry/µm	36	35	34
Thickness soaked/µm	54	46	43
Electrolyte uptake ΔW	248 %	181 %	160 %
Tortuosity τ_{eff}	2.36	3.96	5.18
Conductivity σ (90 °C)/S cm^{-1}	2.7×10^{-4}	1.8×10^{-4}	1.8×10^{-4}
Conductivity σ (20 °C)/S cm^{-1}	5.2×10^{-5}	1.8×10^{-5}	1.2×10^{-5}



FTIR spectra of a porous PVDF-HFP membrane of 8 µm thickness as a pure porous membrane, gel membrane with pure **1**, and gel electrolyte membrane **M-15**.
a) Full spectra;
b) Details of the fingerprint region with marked integrals (black frames) used for FTIR mapping of disiloxane (**1**), TFSI-anion, amorphous framework (*) and its α-phase (α).

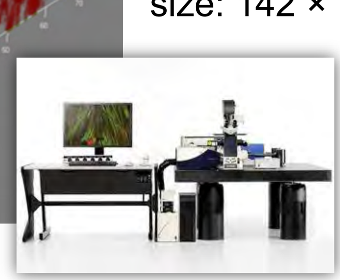


LiTFSI
Lithium-bis(trifluoromethylsulfonyl)imide

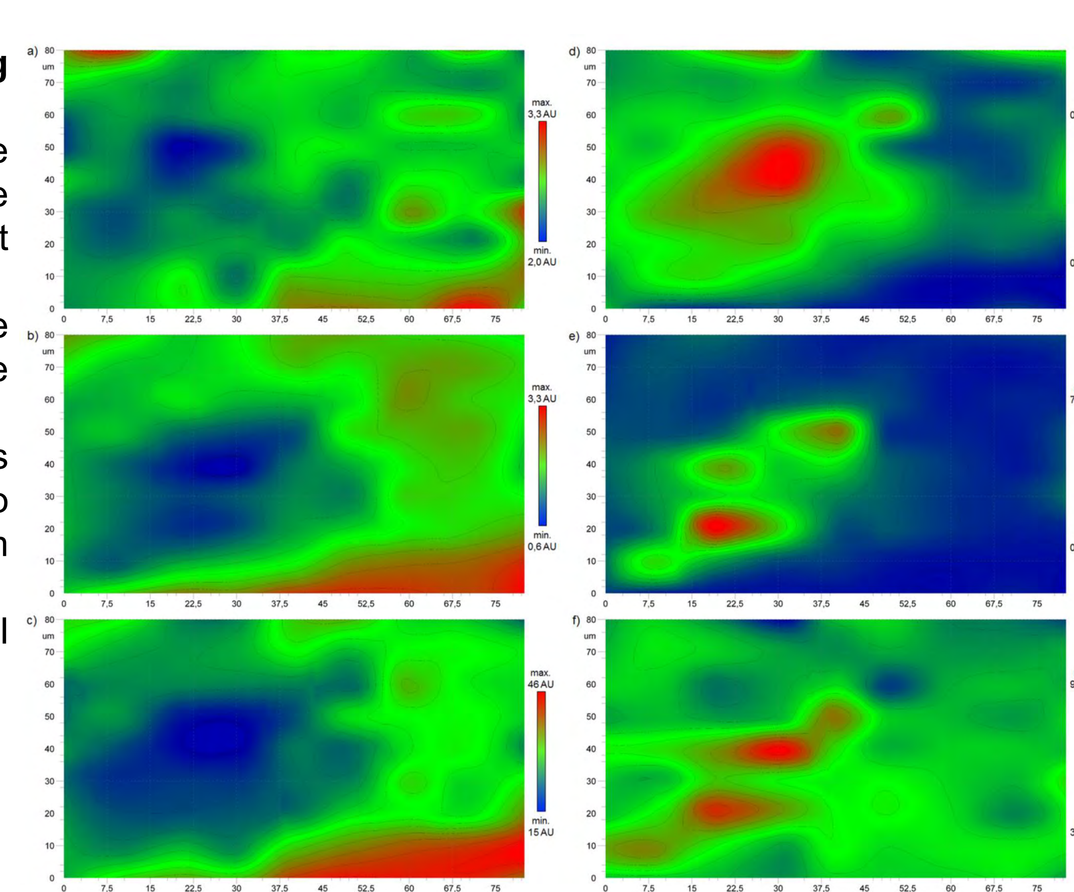


Coherent *anti*-Stokes Raman scattering (CARS) confocal microscopy images
a) Representative optical slice of the surface of a dry, porous PVDF-HFP membrane visualized by exciting the C–H vibration at $\tilde{\nu}$=1430 cm^{-1}.
b) Representative optical slice beneath the surface of **M-5** visualized by exciting the C=O vibration of **1** at $\tilde{\nu}$=1730 cm^{-1}.
c) 3D reconstruction of stacked optical slices of excited C=O vibrations of sample **M-5** to depict a 3D image section of a 12 µm subsurface depth.

Scale bars in relative intensity units; voxel size: 142 × 142 × 420 nm.



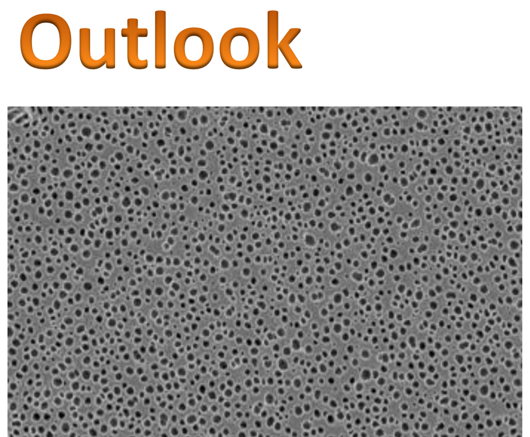
Leica TCS SP8 CARS confocal platform
Label Free Imaging

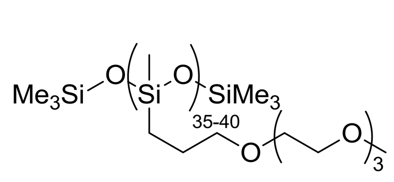


FTIR microscope mapping of a PVDF-HFP gel electrolyte membrane **M-15**.
a) Chemical mapping of PVDF-HFP ($\tilde{\nu}$=865–890 cm^{-1}).
b) SO_2 group in the TFSI-anion ($\tilde{\nu}$=1325–1375 cm^{-1}), C=O group ($\tilde{\nu}$=1715–1770 cm^{-1} region).
c) Si–O–Si stretching and N–CO–O symmetric stretching vibrations ($\tilde{\nu}$=1020–1100 cm^{-1} region).
d) Ratio of the integrated areas between $\tilde{\nu}$=865–890 cm^{-1} (PVDF-HFP) and 1715–1770 cm^{-1} (**1**).
e) Ratio of the integrated areas between $\tilde{\nu}$=865–890 cm^{-1} (PVDF-HFP) and 1325–1375 cm^{-1} (TFSI).
f) Ratio of the integrated areas between $\tilde{\nu}$=1715–1770 (**1**) and 1325–1375 cm^{-1} (TFSI).

AU: arbitrary absorbance unit.

Outlook





PSx-PEO3

Polymeric additive to influence the pore frequency and size of PVDF-HFP membrane.

- Concept of *double active* separators:
  1. Increased uptake of liquid electrolyte (1M LiTFSI in EC/DMC 1:1) up to 500 % by addition of polysiloxane.
  2. Polyether functionalities contribute to ionic transport.
- Reduced degree of crystallinity, increased ionic conductivity (20 wt % PSx-PEO3: 6.4×10^{-4} S cm^{-1} at 20 °C).

Proof of concept

- Synthesis of carbamate-modified polysiloxanes as polymeric additives.
- Interpenetrating networks composed of porous PVDF-HFP and modified polysiloxanes.

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