



# Disiloxanes with a *N*-Propyllic Spacer Group and Cyclic / Non-Cyclic Carbamate Moieties as Plasticizer in Gelled Polymer Electrolytes for Lithium-Ion Batteries



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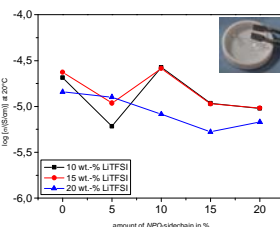
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## Introduction

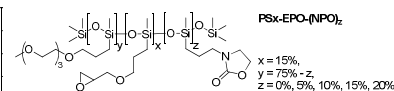
To improve safety of lithium-ion battery systems, solid polymer electrolytes (SPE) are an alternative to commercially used liquid electrolyte blends of organic carbonates. Polysiloxanes are promising for usage in SPEs, due to their flexible Si-O-Si backbone, low glass transition temperatures ( $T_g$ ) and non-toxicity.

As an inexpensive industrial by-product polymethylhydrosiloxane (PMHS) is the starting component of choice in synthesis of versatile modified polysiloxane based macromolecules, which are crosslinked to form ionic conducting membranes.

Polysiloxane based electrolytes, mostly modified with ethylene oxide sidechains, suffer from poor ionic conductivities at room temperature ( $< 10^{-3}$  S/cm). Therefore, polar moieties, e.g. cyclic carbonate and carbamate, were introduced onto the polysiloxane backbone. But ionic conductivity decreased when increasing amounts of *N*-propyl-oxazolidinone (NPO) were incorporated, due to increased dipole-dipole interactions.



ionic conductivity of polysiloxane based SPE membranes  $PS_x-EPO-(NPO)_z$  at 20 °C depending on amount of NPO.

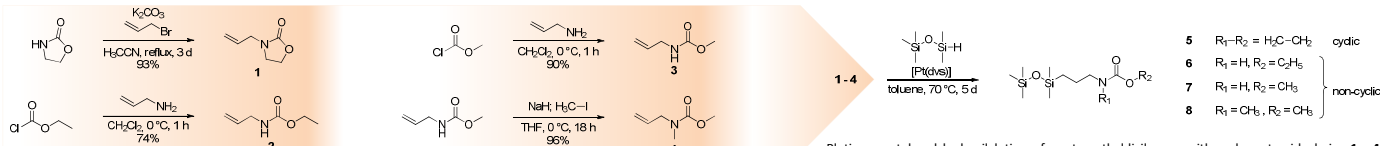


### Model Compounds

Why disiloxane based carbamates?

- To study the influence of the carbamate structure on ionic conductivity  $\sigma$ , viscosity  $\eta$ , relative permittivity  $\epsilon_r$ , and electrochemical stability.
- To suggest optimization directions for tailored improvement.

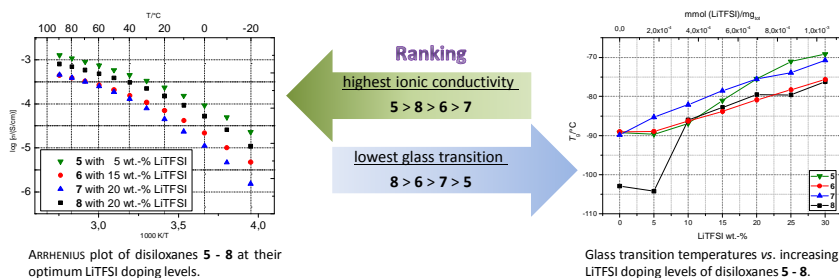
## Synthesis of Disiloxane based Model Compounds



Reactions proceeded efficiently leading to formation of *N*-allylic carbamate sidechains 1-4 in good yields. All products were purified by distillation in vacuum.

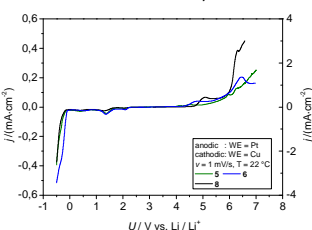
Platinum catalyzed hydrosilylation of pentamethyldisiloxane with carbamate sidechains 1-4. The corresponding disiloxanes 5-8 were purified by chromatography to achieve purity  $> 99.5\%$  (GC-MS) and were dried in vacuum ( $< 20$  ppm water content).

## Characterization of Disiloxanes



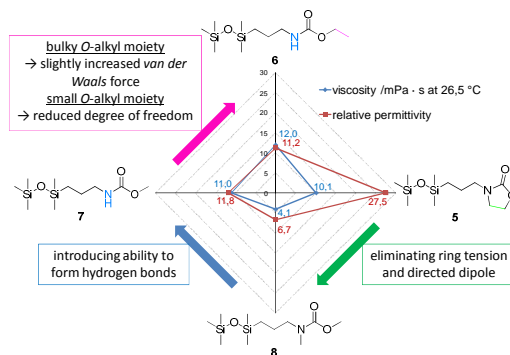
ARRHENIUS plot of disiloxanes 5-8 at their optimum LITFSI doping levels.

- Disiloxane 5 ( $\epsilon_r = 27.5$ ) is like a polar solvent dissolving LITFSI with strong solvent-solute interactions. As a result  $\sigma$  decreases and  $\eta$  increases with higher amounts of Li-salt leading to highest  $T_g$  measured for compared model compounds.
- Disiloxanes 6-8 ( $\epsilon_r = 6.7 - 11.8$ ) are like apolar solvents with weak solvent-solvent and solvent-solute interactions. Due to possible hydrogen bonding 6 and 7 show higher  $\eta$  and lower  $\sigma$  than *N*-methylated 8. Reduced degree of freedom of the *O*-methyl carbamate 7 is consistent with temperature dependence of  $\sigma$  and thermal analysis results.

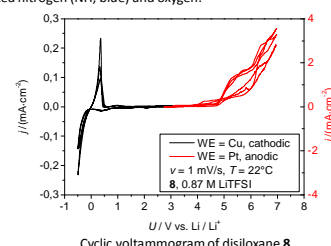


Linear sweep voltammogram of disiloxanes 5-8.

- Electrochemical stability of disiloxanes 5-8 was investigated by linear sweep voltammetry (LSV, left). Oxidative degradation of 5 and 6 commenced at around 4.5 V (vs.  $Li/Li^+$ ). For compound 8 in a potential range between 0 V and 4.8 V (vs.  $Li/Li^+$ ) significant oxidation or reduction was not observed except peaks of water (1.5 V vs.  $Li/Li^+$ ) and copper (0.5 V vs.  $Li/Li^+$ ) reactions.
- Further electrochemical characteristics of disiloxane 8 were measured by cyclic voltammetry (CV, right) showing coulombic efficiency around 57%.
- Coulombic efficiencies of 5 ( $\approx 52\%$ ) and 6 ( $\approx 48\%$ ).



Spider chart illustrating changes in values of viscosity and relative permittivity of disiloxanes 5-8. Structural variations are highlighted, e.g. possible hydrogen bonding sites between non-alkylated nitrogen (NH, blue) and oxygen.



Cyclic voltammogram of disiloxane 8.

## Outlook

- Further optimization of non-cyclic carbamates:
  - Library of different *O*- and *N*-alkylated compounds.
  - Increasing  $\epsilon_r$  and electrochemical stability.
- Transfer of results on SPE synthesis:
  - Introducing cyclic and non-cyclic carbamate moieties onto polysiloxane macromolecules.
- Using disiloxanes as liquid electrolytes:
  - Forming semi-interpenetrating networks by addition of carbamate modified disiloxanes to polymer host materials, e.g. polysiloxanes.

### References

- Zhengcheng Zhang, Leslie J. Lyons, Ryan West, Khalil Amine, Robert West, *Synthesis and ionic conductivity of mixed substituted polysiloxanes with oligoethylene and cyclic carbonate substituents*, *Silicon Chemistry*, 2005, 3, pp. 259-266.

### Acknowledgements:

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