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Ionic transport properties in solid polymer electrolytes: in-plane versus through-plane

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Introduction

Context: Conventional Li-ion batteries can leak and react. [1]. Solution? Replace the liquid electrolyte by a non-flammable dry Solid Polymer Electrolyte (SPE).

Ionic transport properties in SPEs have been largely studied in through-plane (L) configuration. Conversely, in in-plane ($//$) configuration studies are only dedicated to ionic conductivity (σ) of PEO homopolymer doped with a Li salt [2].

Objectives

Goal:

1- Understanding of the transport properties (conductivity σ , transference number t^+ and diffusion D) according to chains morphology, nanostructuration or ionic clusters.

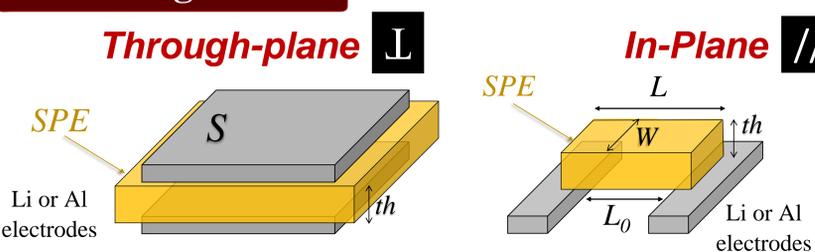
2- Develop methodology to measure the transport properties in through-plane ($//$) vs. in-plane (L).

Experiments: Measurements of various SPEs:

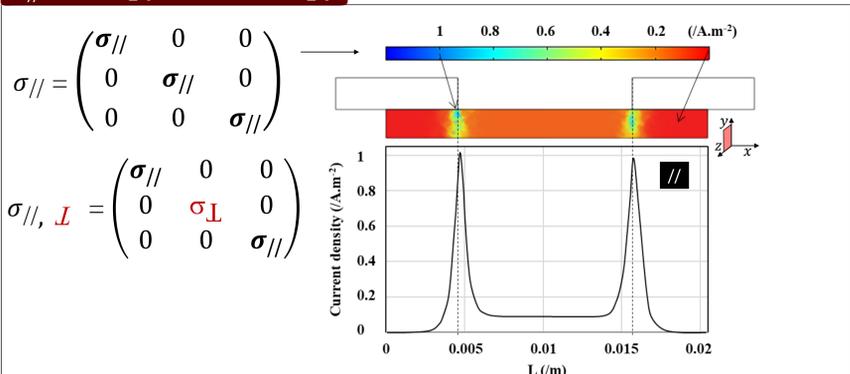
- Homopolymer of PEO/LiTFSI
- Copolymer based on PS-PEO-PS
- Single-ion SPE crosslinked-silica hybrid PEO Vinyl-TFSILi (SI-CHSPE)

Comsol modeling: Difference of potential (conductivity); relaxation of concentration gradients after a polarization step in $//$ and L .

Cell configurations



$\sigma_{//}$ isotropy vs anisotropy

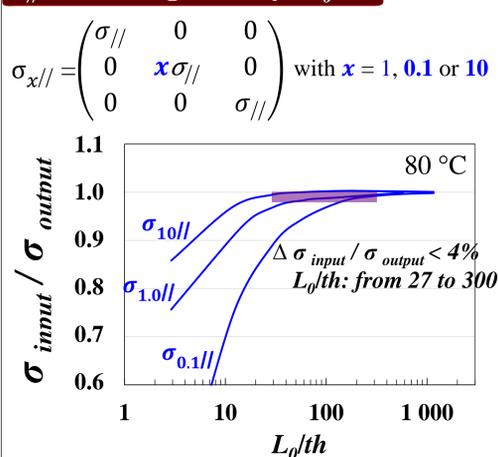


Temperature (°C)	Input (S.cm ⁻¹)	Output $\sigma_{//}$
80	$\sigma_{//} = 1.02 \cdot 10^{-3}$	$1.01 \cdot 10^{-3}$
	$\sigma_{\perp} = 5.67 \cdot 10^{-4}$	
45	$\sigma_{//} = 2.62 \cdot 10^{-5}$	$2.60 \cdot 10^{-5}$
	$\sigma_{\perp} = 1.55 \cdot 10^{-5}$	

- Current density localized at the edge of the electrodes
- Constant ionic current in the SPE cross section

Cell constant: $k_{//} = \frac{L}{w \cdot th}$

$\sigma_{//}$ effect of geometry (L_0/th)



Our results demonstrate $\sigma_{output} = \sigma_{input}$ within < 4% of standard deviation

$\Delta U(t)$, C , D_{amb}

Nernst relation for a salt LiTFSI:
 $\Delta U(t) = \frac{RT}{F} \ln \left(\frac{c^+}{c^-} \right)$

2° Fick law:

$$\frac{\partial C}{\partial t}(x, t) - D_{amb} \frac{\partial^2 C}{\partial x^2}(x, t) = 0$$

$$\Rightarrow \ln(\Delta U) \propto \ln \left(\ln \left(\frac{c^+}{c^-} \right) \right) \propto D_{amb}$$

σ , t^+ & $D^+ + D^-$

Nernst-Einstein equation:

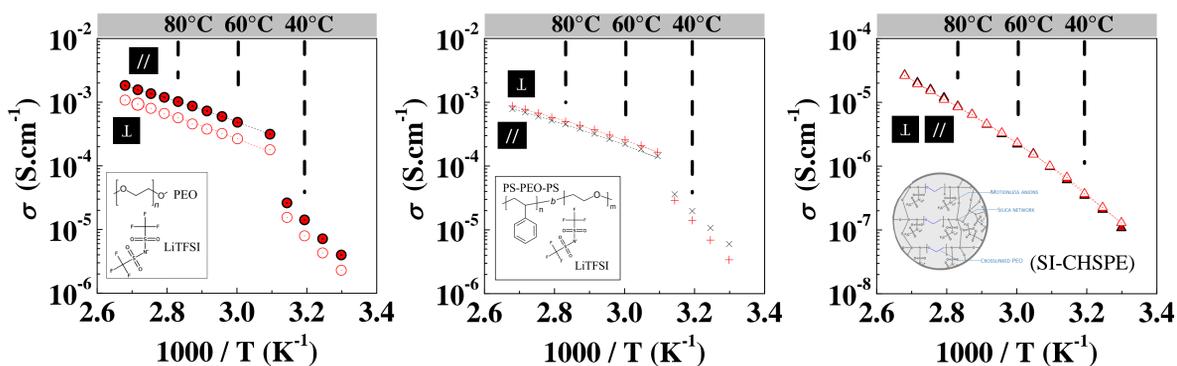
$$\sigma = \frac{F^2 (D^+ + D^-) \alpha C_{Li \text{ salt}}}{RT}$$

With α , dissociation rate of the SPE
 $C_{Li \text{ salt}}$: concentration of the lithium salt

$$\begin{cases} D^- = \frac{D_{amb}}{2t^+} \\ D^+ = \frac{D_{amb}}{2(1-t^+)} \end{cases}$$

Ionic conductivity $\sigma_{//} \neq \sigma_{\perp}$: why?

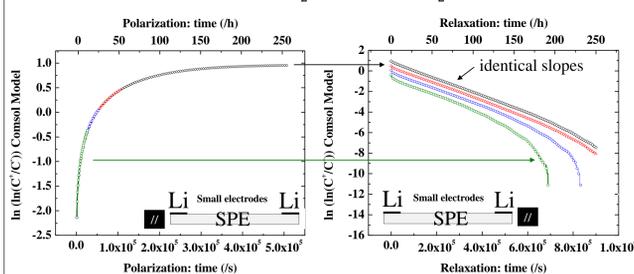
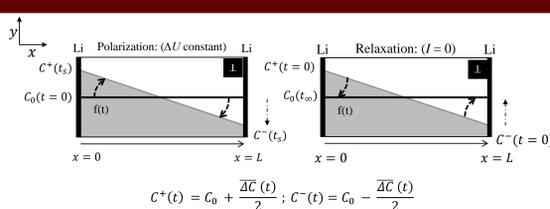
The SPE electrolyte resistance R_{el} is determined by Electrochemical Impedance Spectroscopy (EIS) [3] $\sigma = \frac{k}{R_{el}}$



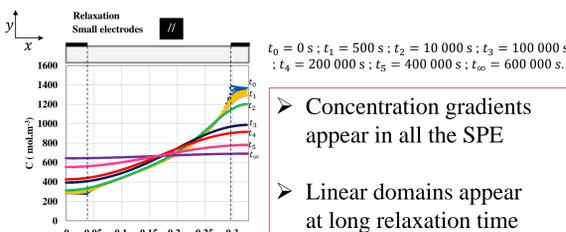
M_w (kg.mol ⁻¹)	PEO	PS-PEO-PS	Single-ion SPE: CHSPE
EO/Li = 25	250-400k	6.7k-35k-6.7k	CHSPE
$\sigma_{//} / \sigma_{\perp}$ at 80°C	1.80 ± 0.05	0.91 ± 0.02	0.98 ± 0.02

\neq anisotropy according to the materials structuration

Polarization / Relaxation

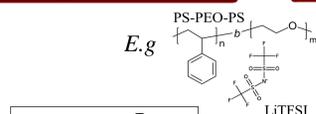


In $//$, waiting the total polarization of the cell to measure **only** D_{amb} $//$ is not essential



- Concentration gradients appear in all the SPE
- Linear domains appear at long relaxation time

Transport number

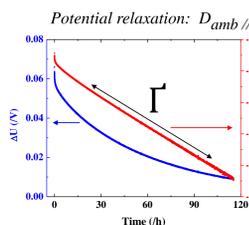
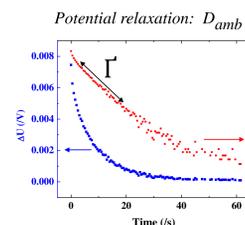
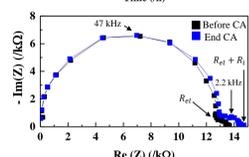
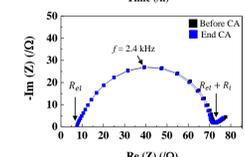
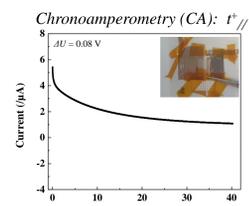
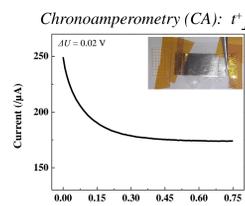


$$t_{L \text{ or } //}^+ = \frac{R_{el}}{V - R_s}$$

Diffusion

$$D_{amb \perp} = \frac{\Gamma th^2}{\pi^2}$$

Watanabe method (CA) [4] Newman method (OCV) [5]



Transport properties - Conclusion

- In PEO and PS-PEO, anisotropy mainly due to the variation of D^+ and impact of transference number t^+
- The anisotropy experimentally measured may due to chain morphology along L and $//$
- In L for single-ion conductors, the passivation layers play a main role in the t^+ determination

M_w (kg.mol ⁻¹)	PEO	PS-PEO-PS	Single-ion SPE: CHSPE
EO/Li = 25	250-400k	6.7k-35k-6.7k	CHSPE
$\frac{t^+_{//}}{t^+_{\perp}}$	1.69 ± 0.02	1.23 ± 0.02	$t^+_{//} = 1 \pm 0.02$ $t^+_{\perp} = 0.89 \pm 0.01$
$\frac{D^-_{//}}{D^-_{\perp}}$	1.60 ± 0.01	0.88 ± 0.01	--
$\frac{D^+_{//}}{D^+_{\perp}}$	3.20 ± 0.01	1.08 ± 0.02	--
$\frac{D^+ + D^-_{//}}{D^+ + D^-_{\perp}}$	1.80 ± 0.02	0.91 ± 0.02	--

References

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