



HAL
open science

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

Roselyne Jeanne-Brou, Jonathan Deseure, Didier Devaux, R. Bouchet

► To cite this version:

Roselyne Jeanne-Brou, Jonathan Deseure, Didier Devaux, R. Bouchet. Ionic transport properties in solid polymer electrolytes: in-plane versus through-plane. Journée Scientifique PEM - ED, Oct 2021, Grenoble, France. hal-03793928

HAL Id: hal-03793928

<https://hal.science/hal-03793928>

Submitted on 2 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

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

Roselyne Jeanne-Brou, Jonathan Desseure, Renaud Bouchet, Didier Devaux

Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI (France) –
roselyne.jeanne-brou@grenoble-inp.fr / renaud.bouchet@grenoble-inp.fr / didier.devaux@grenoble-inp.fr

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.

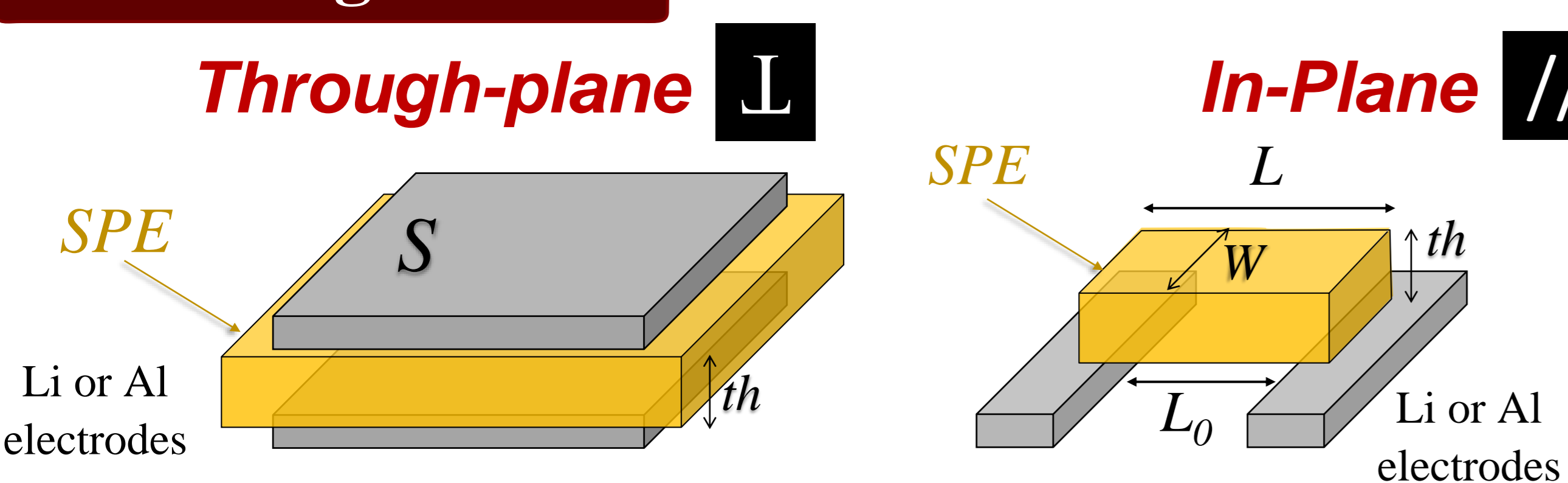
2- Develop methodology to measure the transport properties in through-plane ($//$) vs. in-plane (L).

Experiments: Measurements of various SPEs:

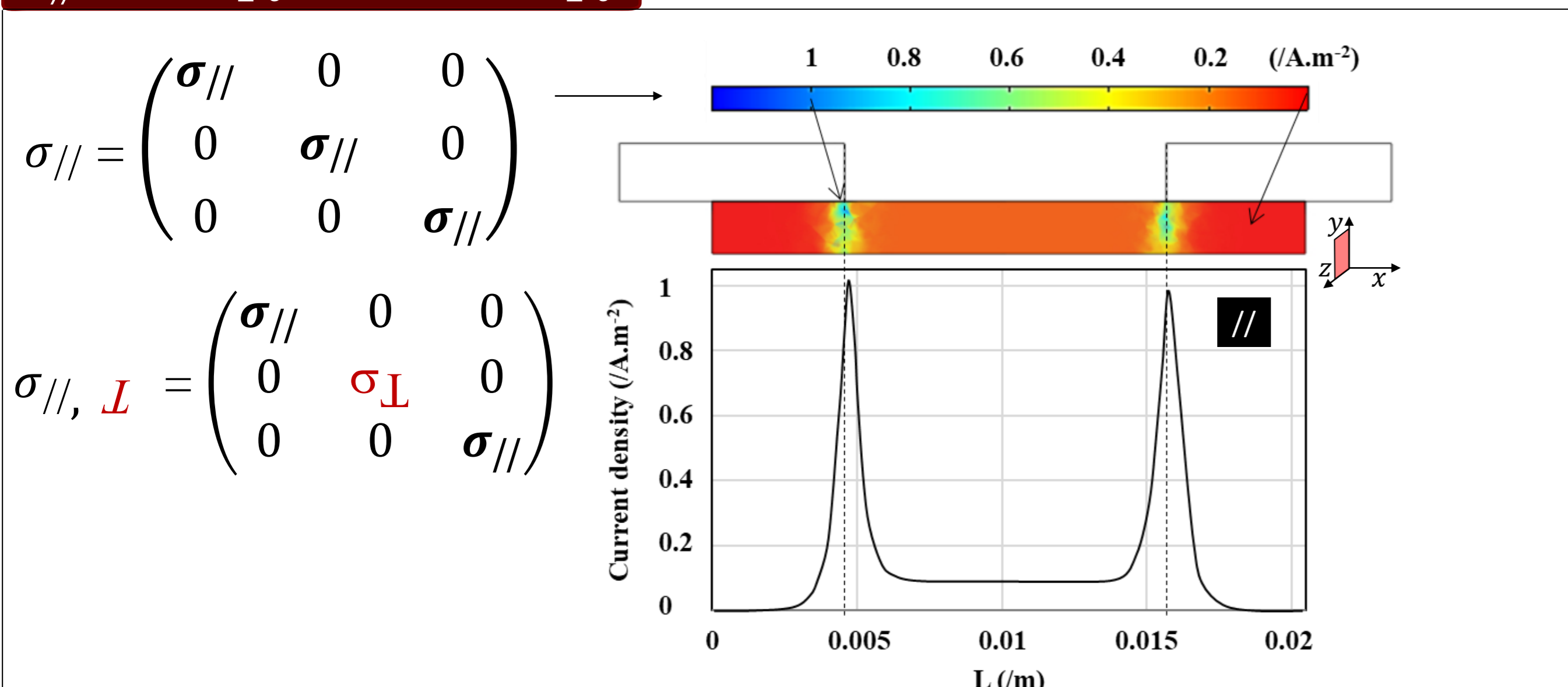
- Homopolymer of PEO/LiTFSI
- Copolymer based on PS-PEO-PS
- Single-ion SPE crosslinked-silica hybrid PEO Vinyl-TFSILi (SI-CHSPE)

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

Cell configurations



$\sigma_{//}$ isotropy vs anisotropy

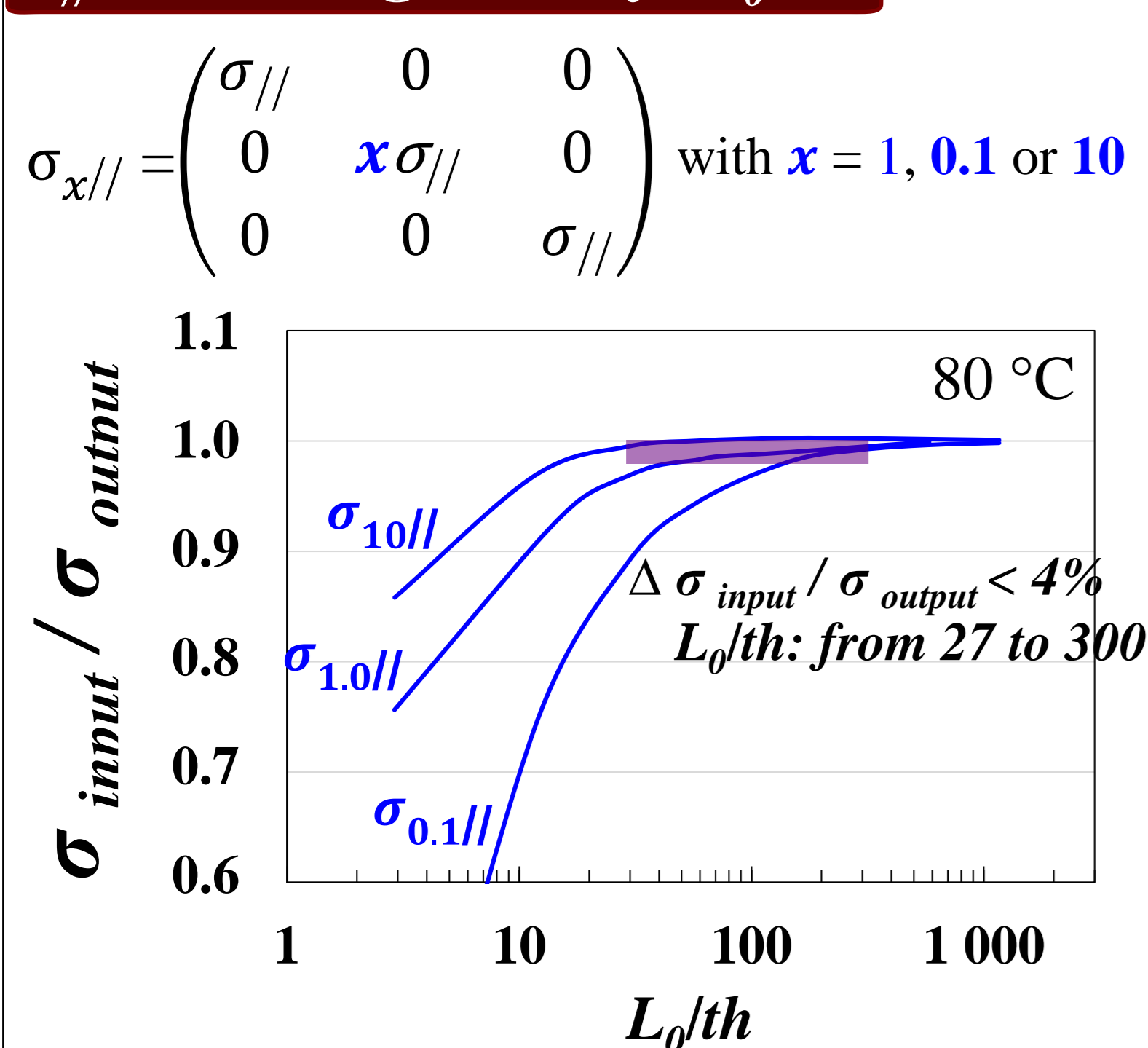


Temperature (°C)	Input (S.cm ⁻¹)	Output $\sigma_{//}$
80	$\sigma_{//} = 1.02 \cdot 10^{-3}$	$1.01 \cdot 10^{-3}$
	$\sigma_{\perp} = 5.67 \cdot 10^{-4}$	
45	$\sigma_{//} = 2.62 \cdot 10^{-5}$	$2.60 \cdot 10^{-5}$
	$\sigma_{\perp} = 1.55 \cdot 10^{-5}$	

- 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^o 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:

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

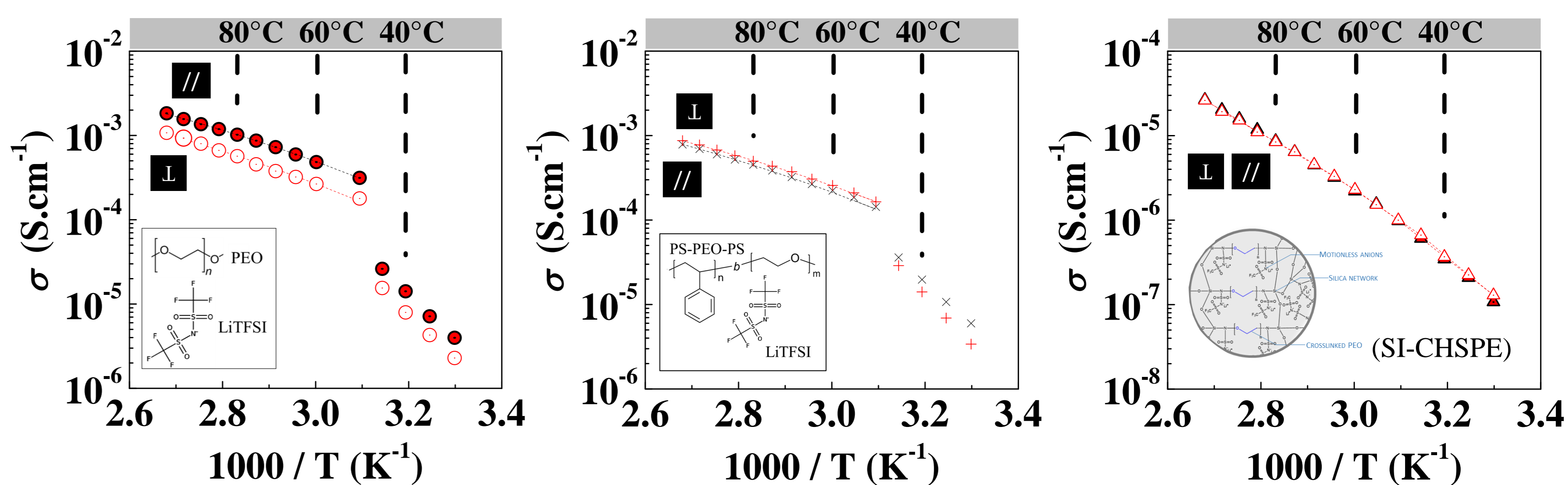
With α , dissociation rate of the SPE
 $C_{Li \text{ salt}}$: concentration of the lithium salt

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

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

The SPE electrolyte resistance R_{el} is determined by Electrochemical Impedance Spectroscopy (EIS) [3]

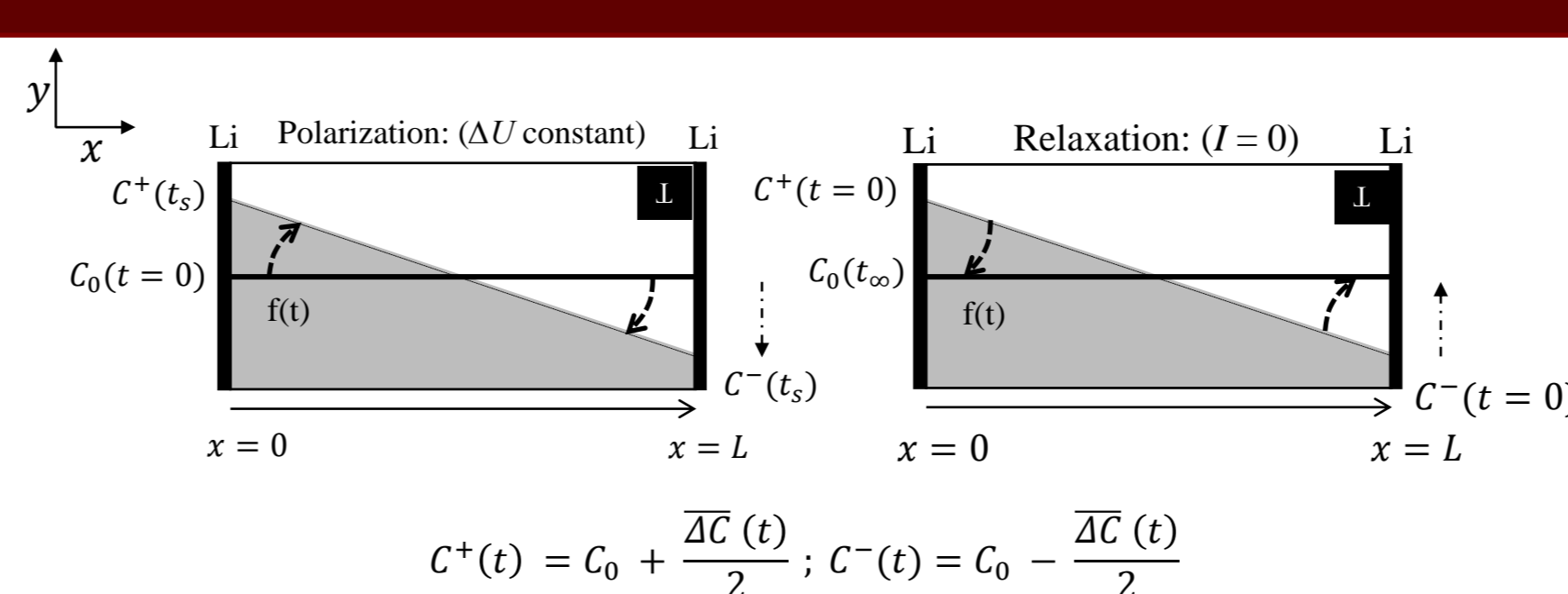
$$\sigma = \frac{k}{R_{el}}$$



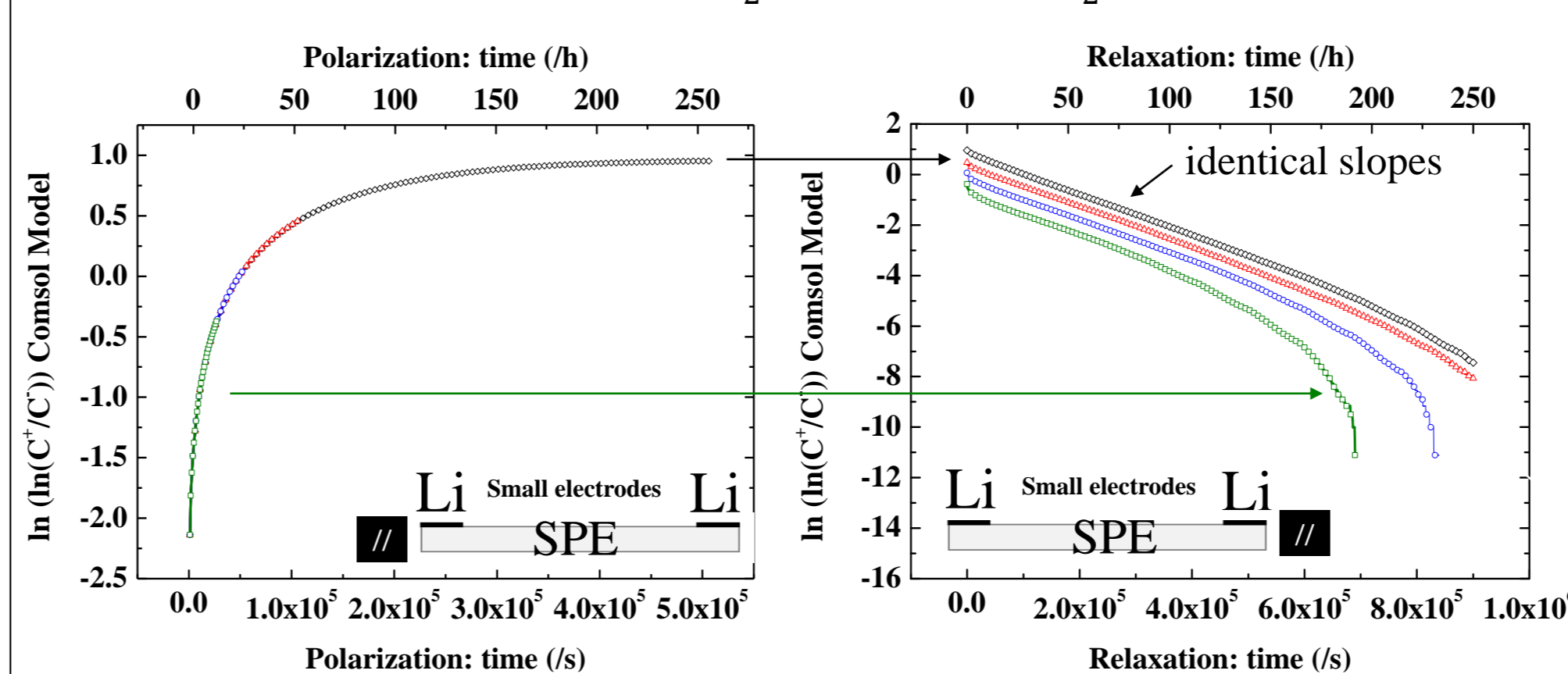
M_w (kg.mol ⁻¹)	PEO	PS-PEO-PS	Single-ion SPE: CHSPE
EO/Li = 25	250-400k	6.7k-35k-6.7k	CHSPE
$\sigma_{//} / \sigma_{\perp}$ at 80°C	1.80 ± 0.05	0.91 ± 0.02	0.98 ± 0.02

\neq anisotropy according to the materials structuration

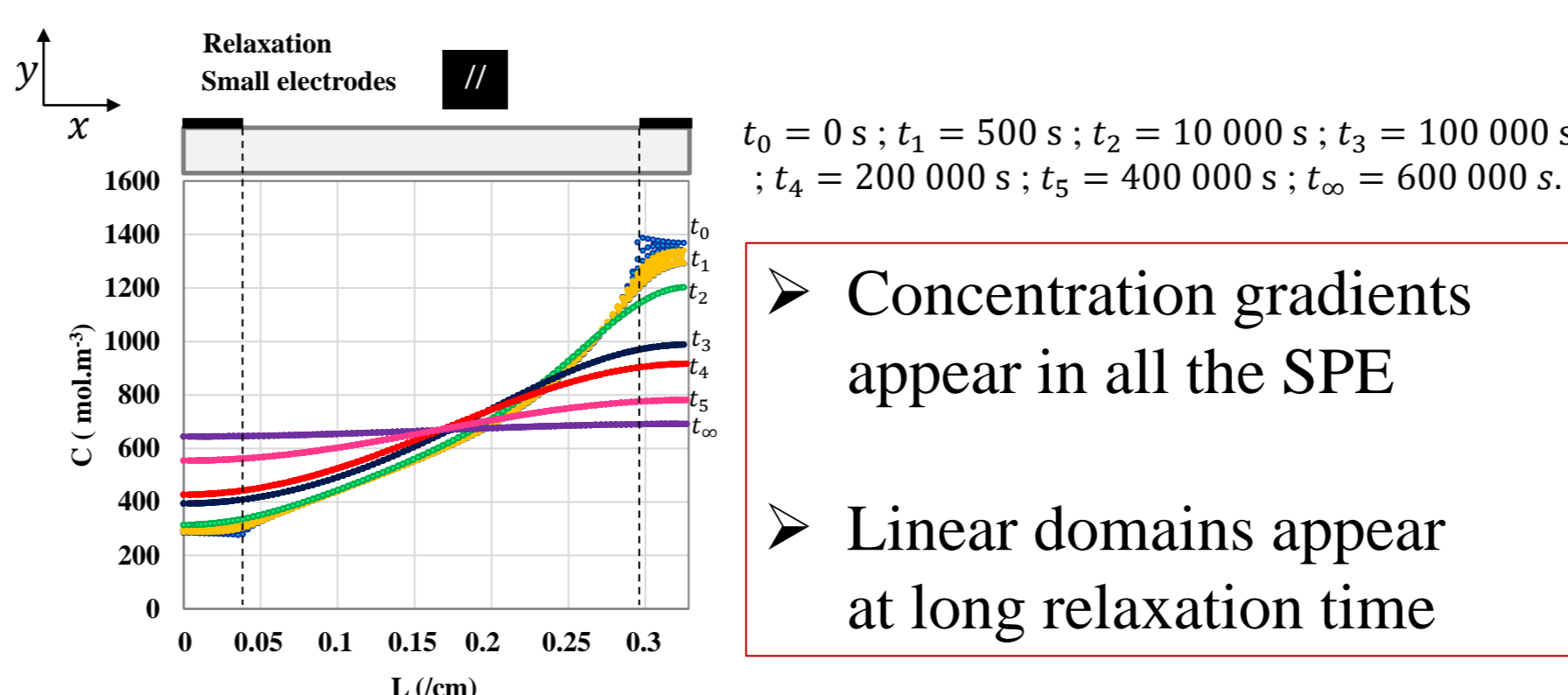
Polarization / Relaxation



$$C^+(t) = C_0 + \frac{\Delta C}{2}; C^-(t) = C_0 - \frac{\Delta C}{2}$$



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

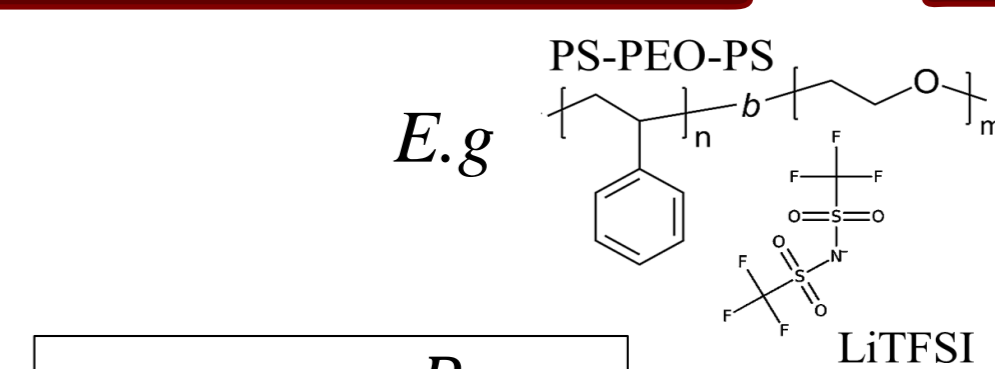


Concentration gradients appear in all the SPE

Linear domains appear at long relaxation time

Transport number

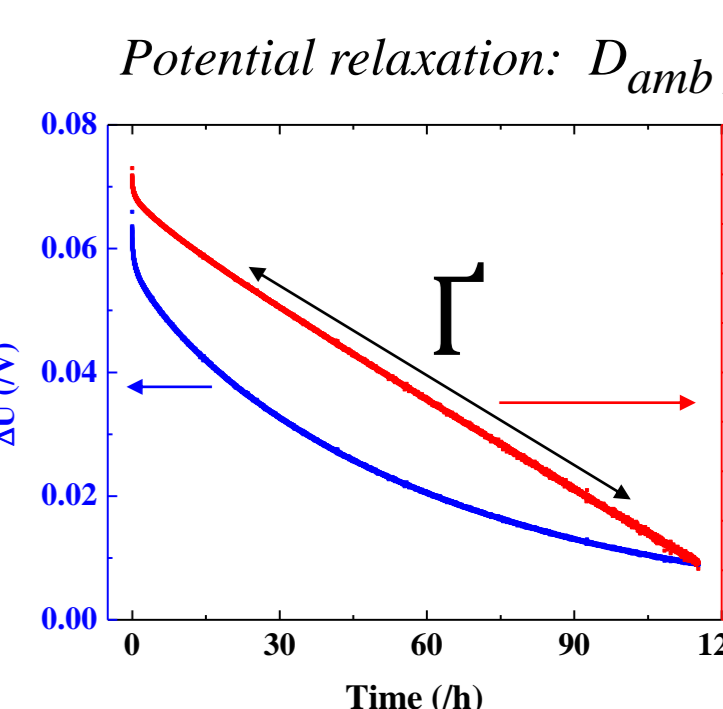
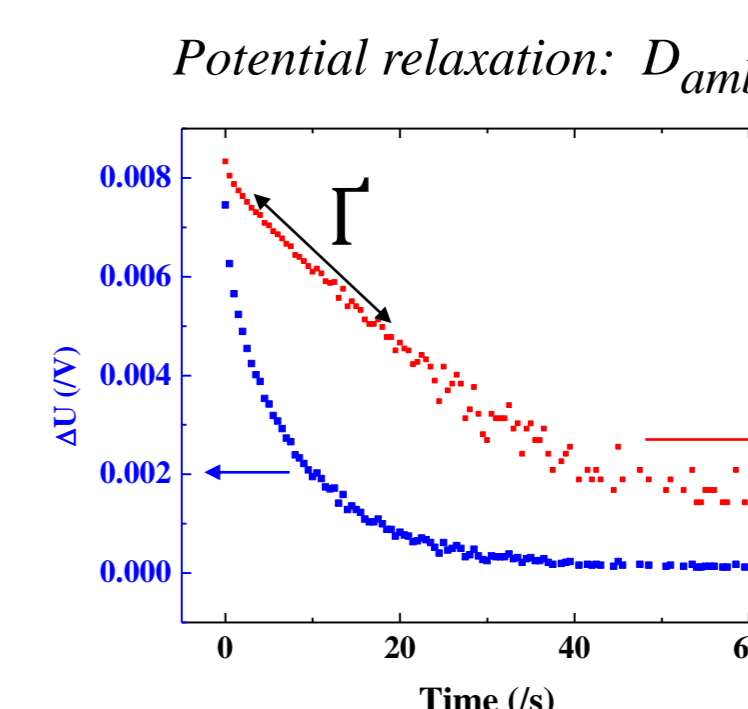
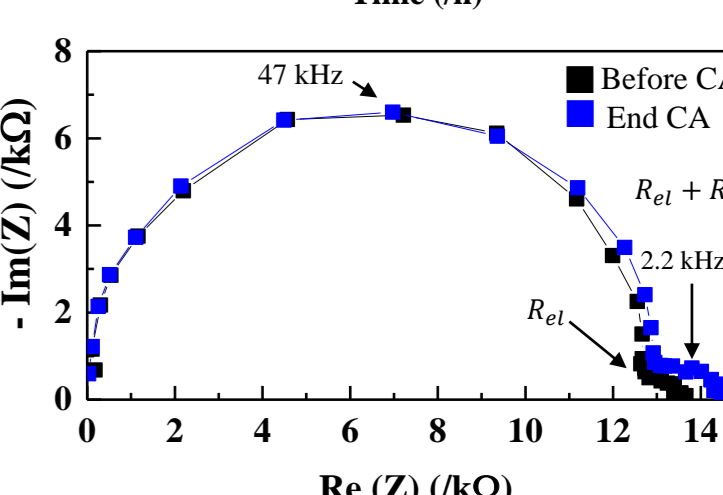
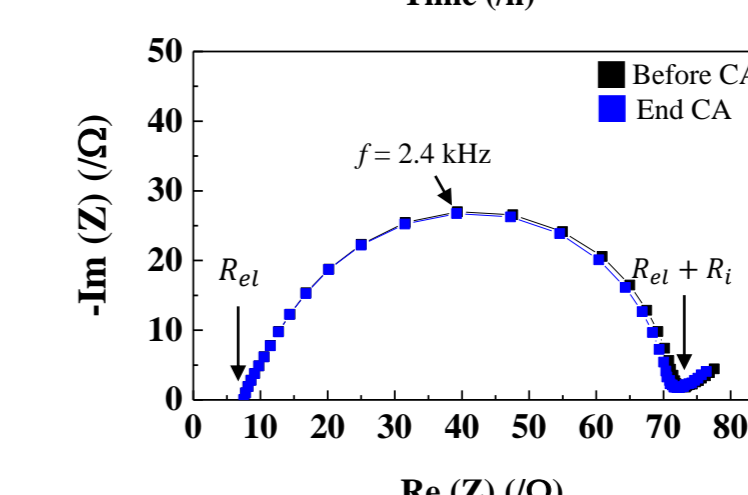
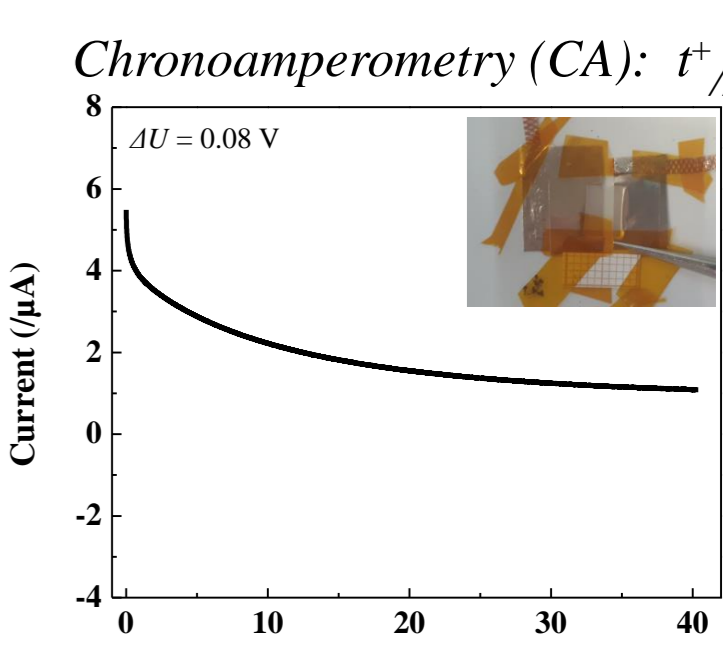
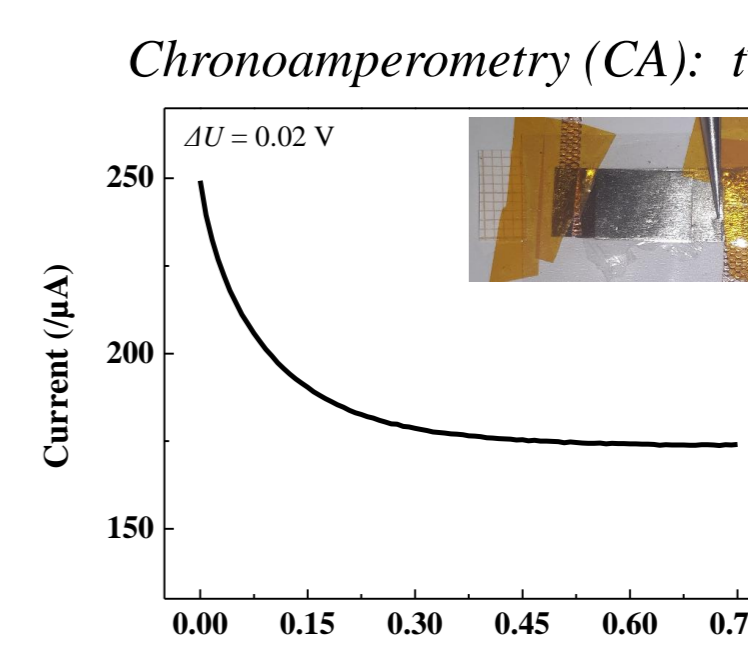
Diffusion



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

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

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

- D. Lisbona, T. Snee, *Process Saf. Environ.*, 89, 434 (2011).
- D. Golodnitsky and E. Peled, *Electrochimica Acta*, 45, 1431-1436 (2000)
- R. Bouchet et al. *J. Electrochem. Soc.*, 150, A1385 (2003).
- M. Watanabe et al. *Solid State Ion.*, 28-30, 911-917 (1988).
- S. D. Thompson and J. Newman, *J. Electrochem. Soc.*, 136, 3362 (1989)