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

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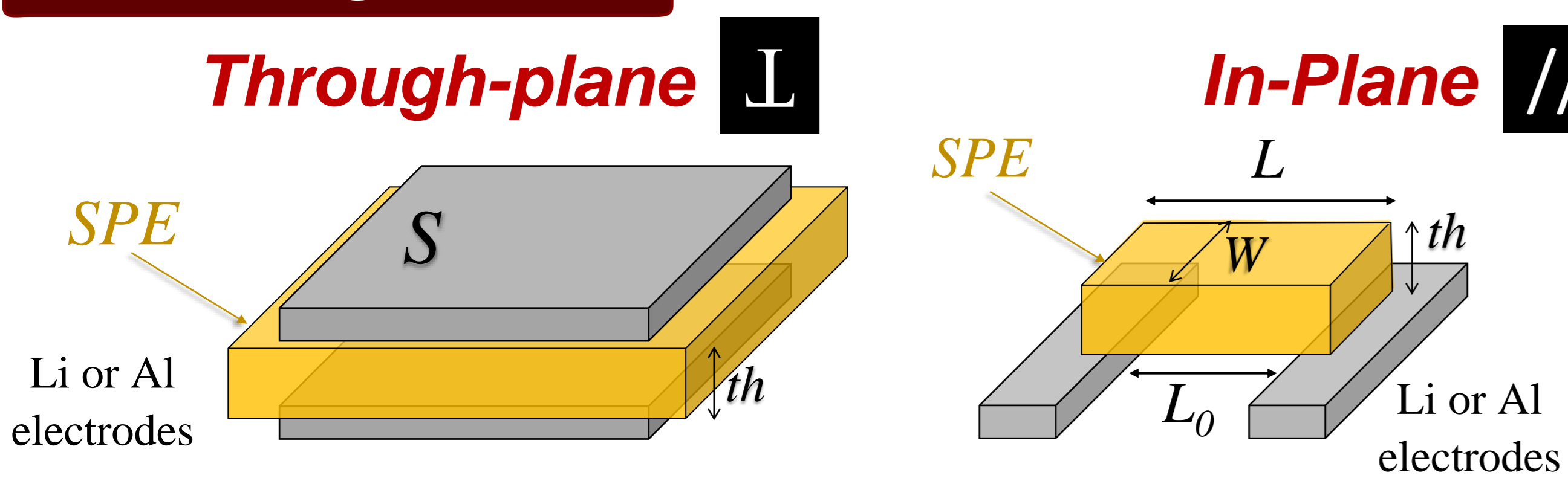
## Introduction

- 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 ( $\sigma$ ) of PEO homopolymer doped with a Li salt [2].

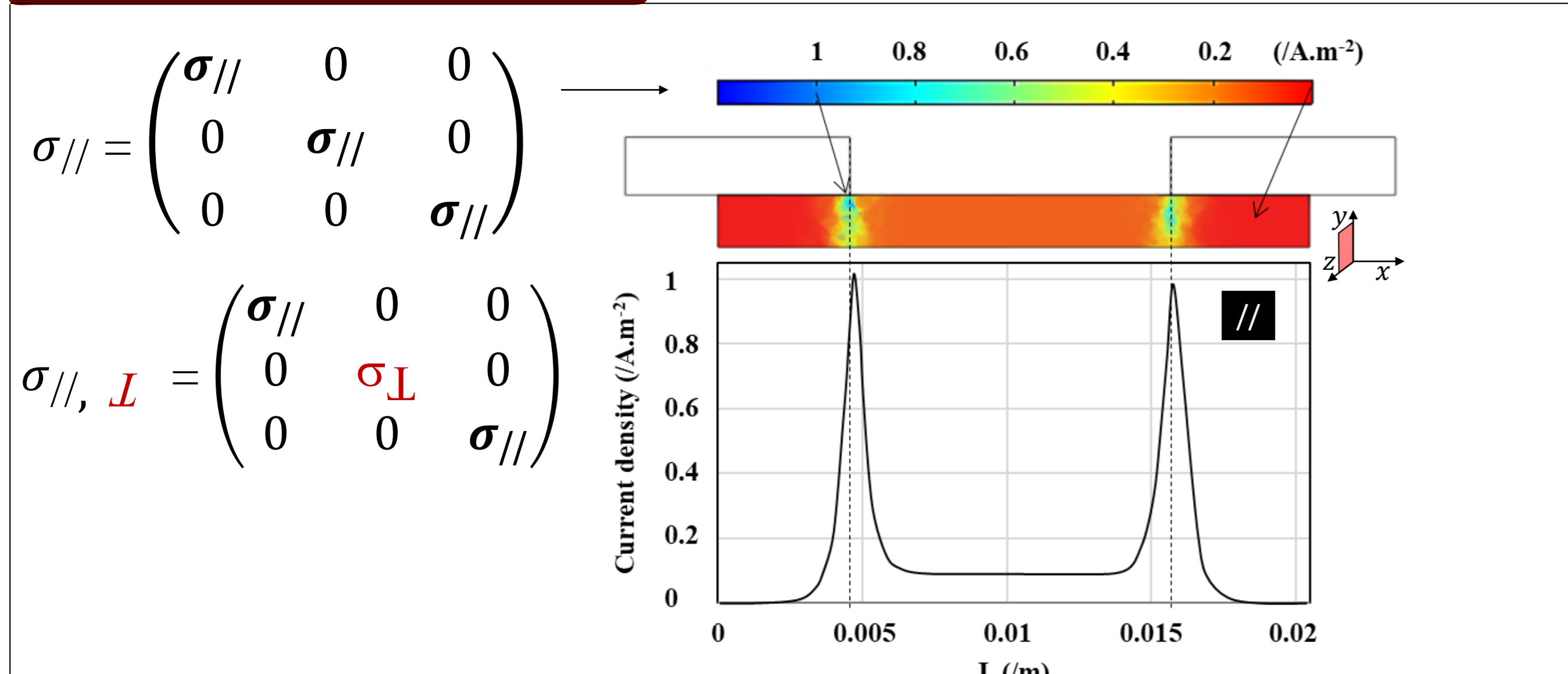
## Objectives

- Goal:**
  - Understanding of the transport properties (**conductivity  $\sigma$ , transference number  $t^+$  and diffusion  $D$** ) according to **chains morphology, nanostructuration or ionic clusters**.
  - 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



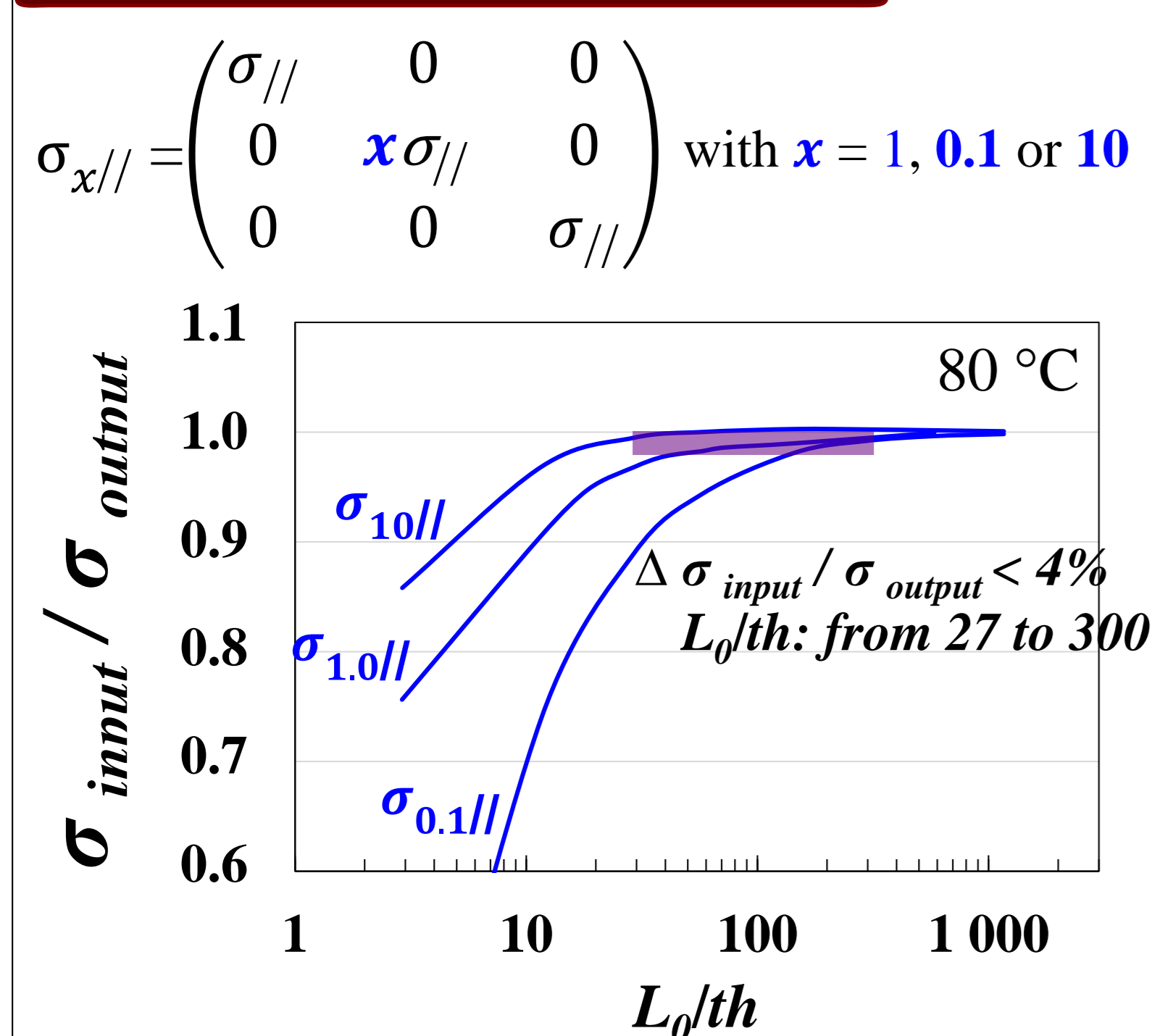
## $\sigma_{//}$ isotropy vs anisotropy



Temperature (°C)	Input (S.cm <sup>-1</sup> )	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<sup>o</sup> Fick law:  
 $\frac{\partial C}{\partial t}(x, t) - D_{amb} \frac{\partial^2 C}{\partial x^2}(x, t) = 0$   
 $\Rightarrow \ln(\Delta U) \propto \ln \left( \ln \left( \frac{c^+}{c^-} \right) \right) \propto D_{amb}$

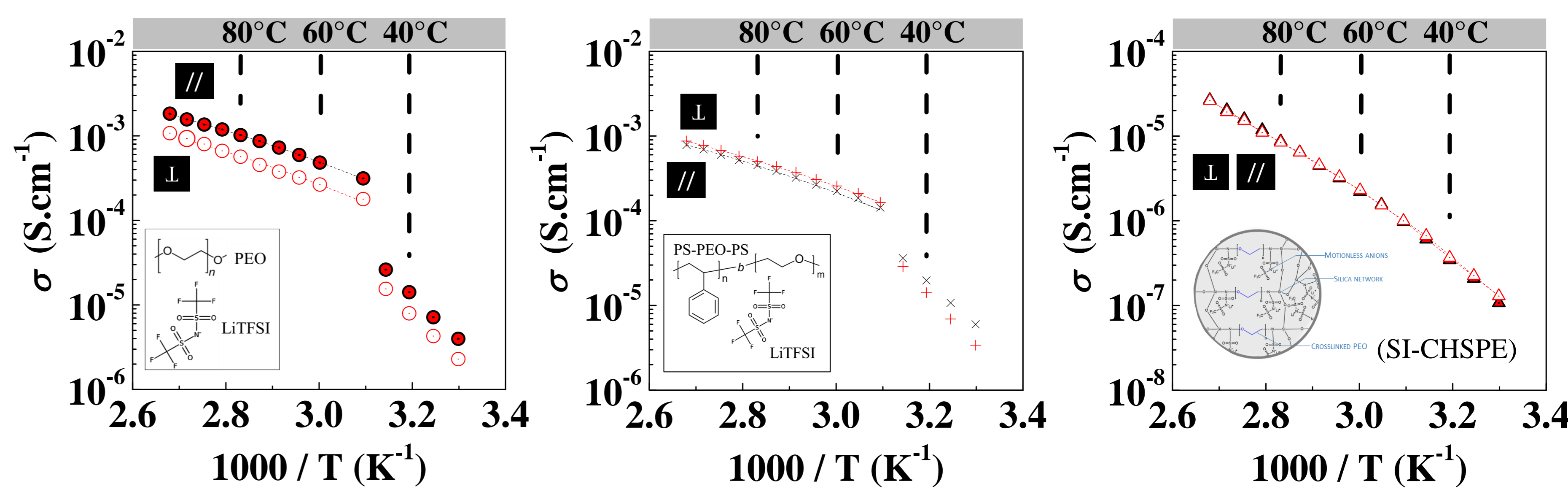
## $\sigma$ , $t^+$ & $D^+ + D^-$

Nernst-Einstein equation:  
 $\sigma = \frac{F^2 (D^+ + D^-) \alpha C_{Li \text{ salt}}}{RT}$   
With  $\alpha$ , 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?

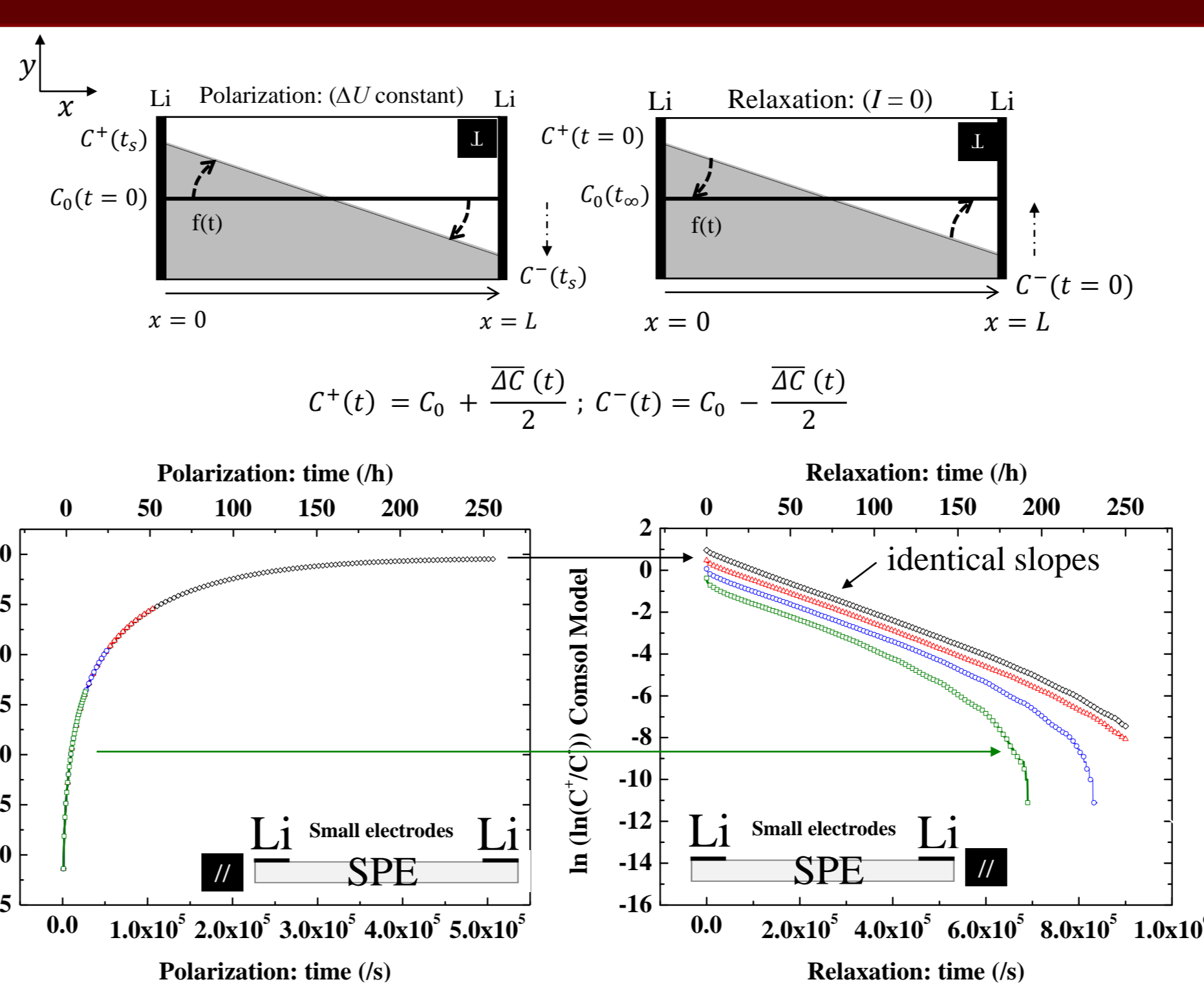
The SPE electrolyte resistance  $R_{el}$  is determined by Electrochemical Impedance Spectroscopy (EIS) [3]  $\sigma = \frac{k}{R_{el}}$



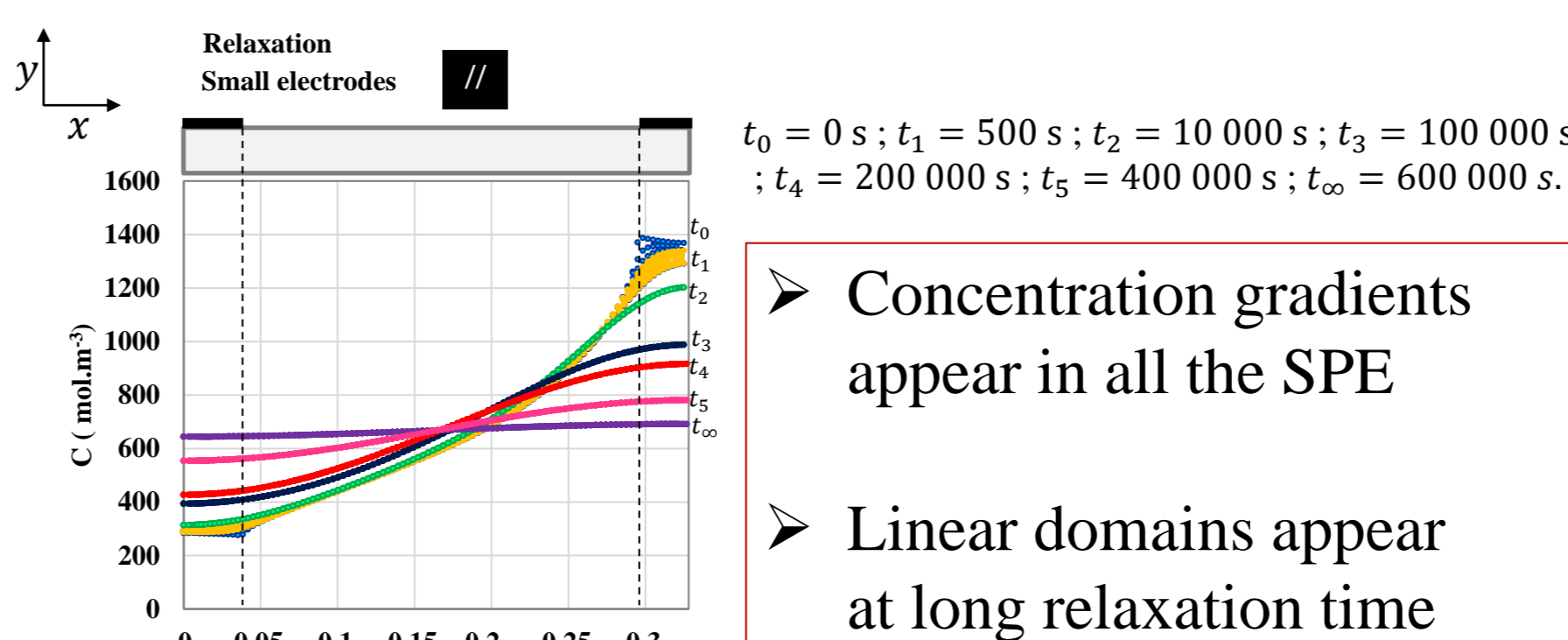
$M_w$ (kg.mol <sup>-1</sup> )	PEO	PS-PEO-PS	Single-ion SPE: CHSPE
EO/Li = 25	250-400k	6.7k-35k-6.7k	
$\sigma_{//} / \sigma_{\perp}$ at 80°C	$1.80 \pm 0.05$	$0.91 \pm 0.02$	$0.98 \pm 0.02$

$\neq$  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

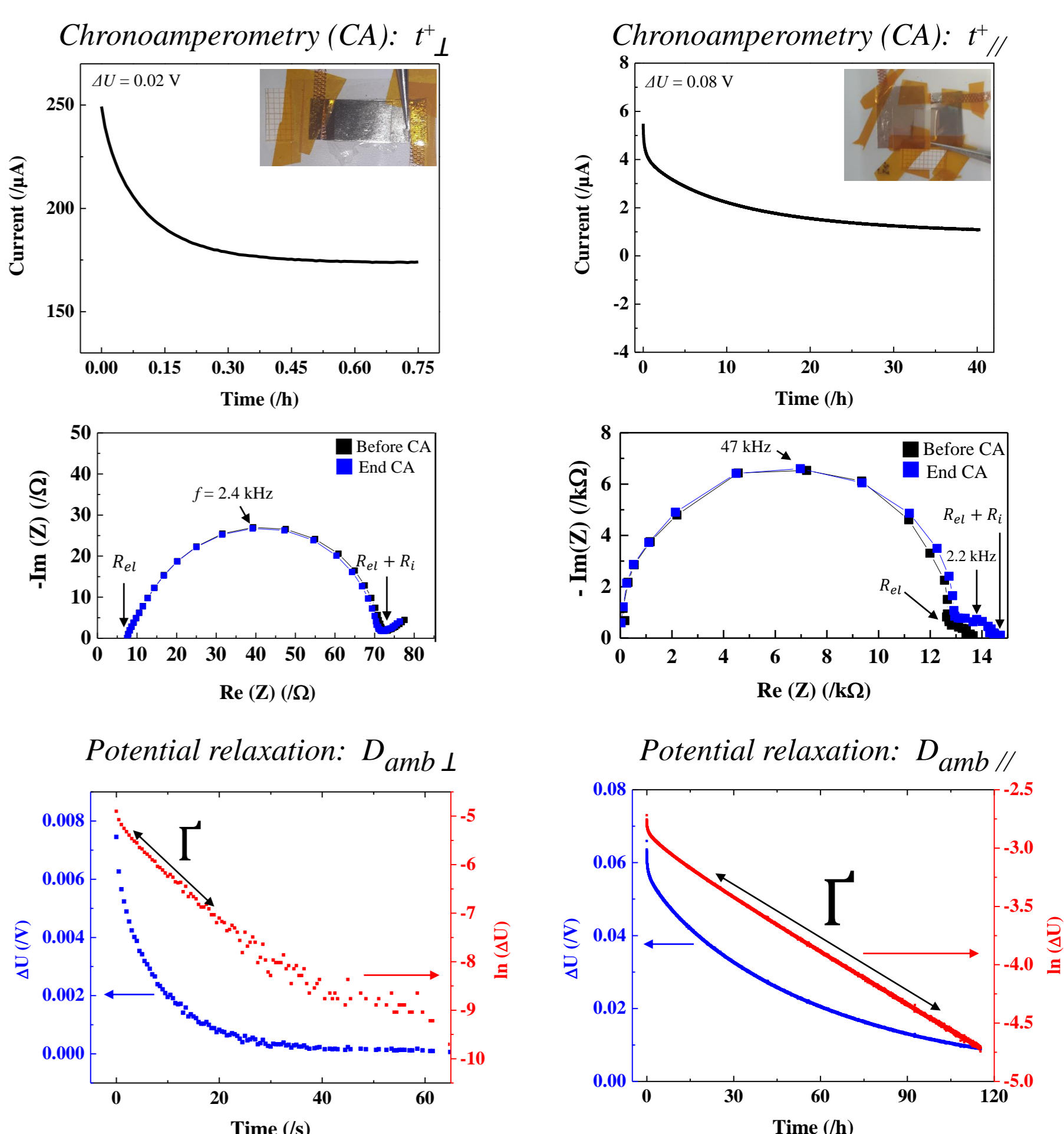
## Transport number

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

## 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 <sup>-1</sup> )	PEO	PS-PEO-PS	Single-ion SPE: CHSPE
EO/Li = 25	250-400k	6.7k-35k-6.7k	
$\frac{t^+ //}{t^+ \perp}$	$1.69 \pm 0.02$	$1.23 \pm 0.02$	$t^+ // = 1 \pm 0.02$ $t^+ \perp = 0.89 \pm 0.01$
$\frac{D^- //}{D^- \perp}$	$1.60 \pm 0.01$	$0.88 \pm 0.01$	--
$\frac{D^+ //}{D^+ \perp}$	$3.20 \pm 0.01$	$1.08 \pm 0.02$	--
$\frac{D^+ + D^- //}{D^+ + D^- \perp}$	$1.80 \pm 0.02$	$0.91 \pm 0.02$	--

## References

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