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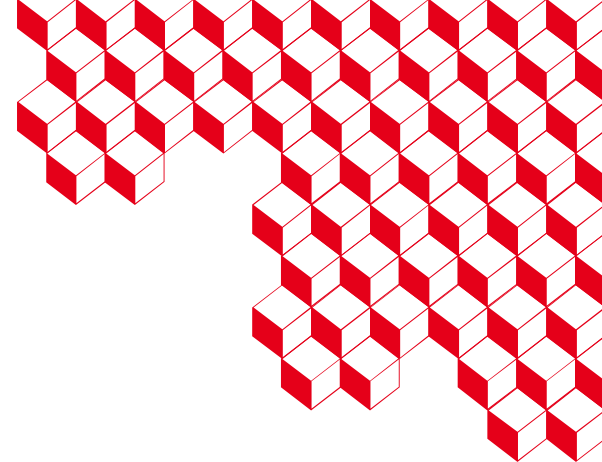
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Carbonate-based single-ion polymer electrolytes for lithium batteries

Chloé FARINA¹, Laurent BERNARD¹, Matthieu LANDA¹, Nicolas LECONTE², Lionel PICARD¹

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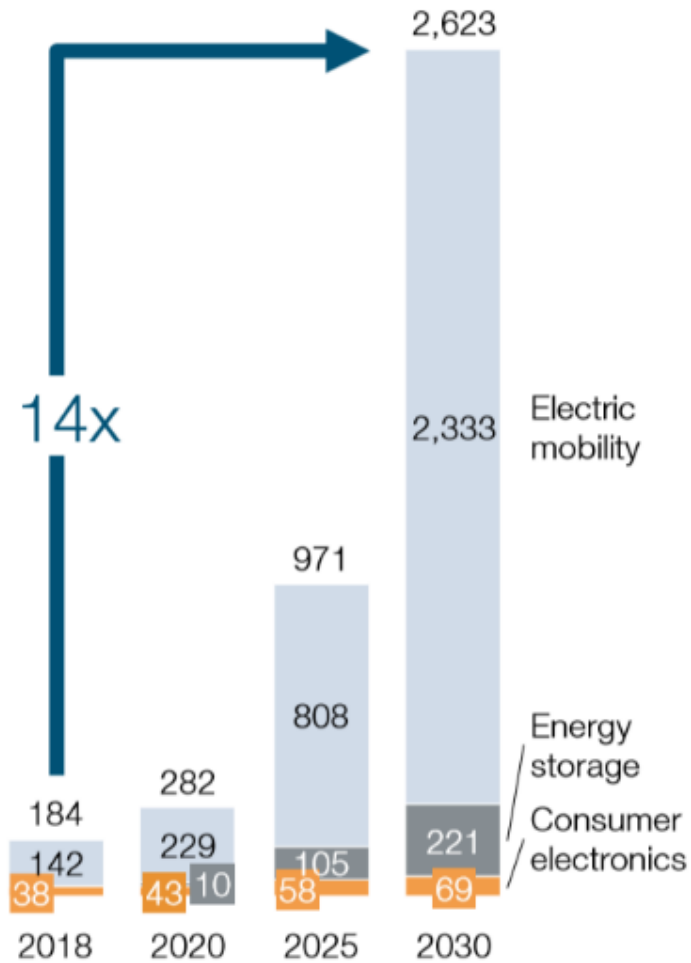
² Univ. Grenoble Alpes, Department of Molecular Chemistry, 38000 Grenoble, France



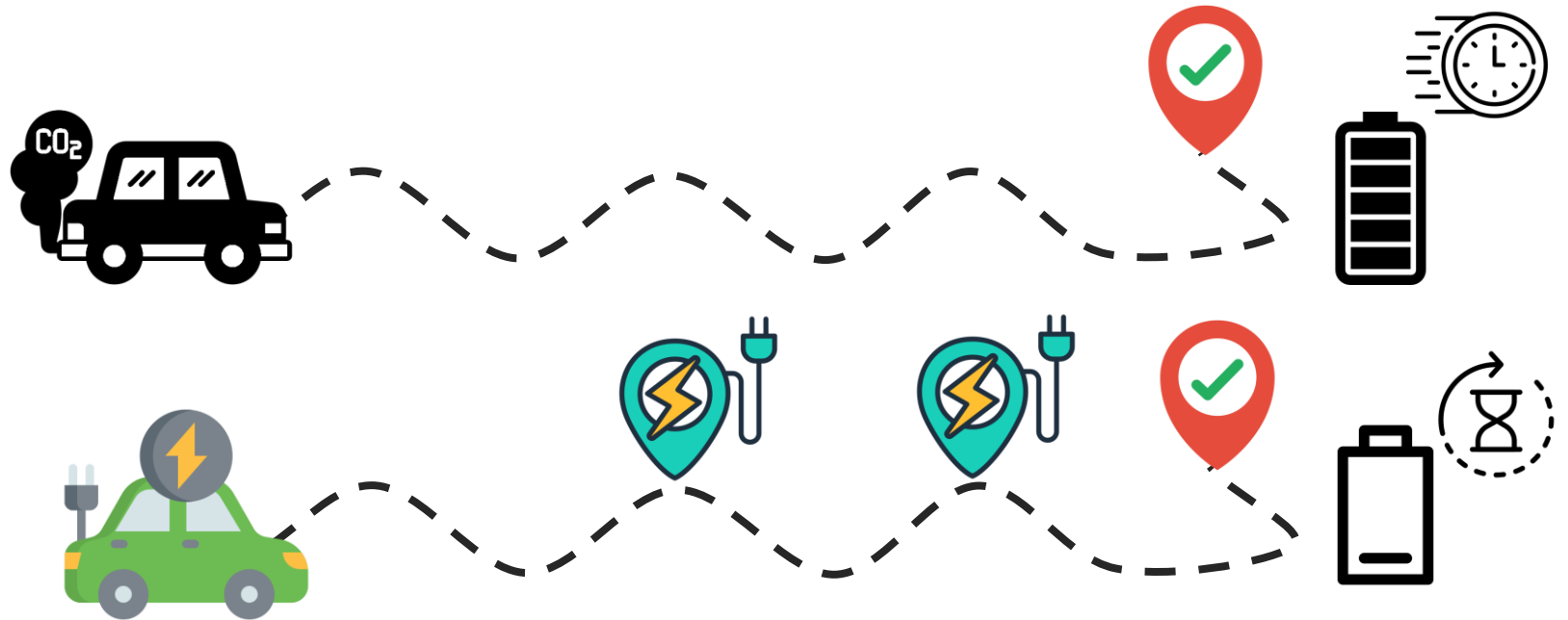
chloe.farina@cea.fr



Context



Estimated worldwide demand for batteries by application by 2030 (GWh) ^[1]



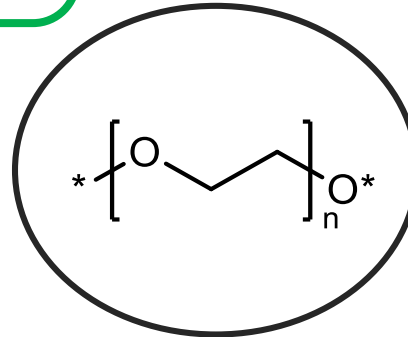
Challenges

- ❑ Need of **very high energy density** batteries
- ❑ Develop polymers with **high electrochemical stability** (Li-metal // NMC)

Polymer electrolytes: PEO

► Li⁺ Conductivities

- Ionic conductivity about **1 mS.cm⁻¹ at 80°C**
- Low glass-transition temperature ($T_g = -60^\circ\text{C}$)



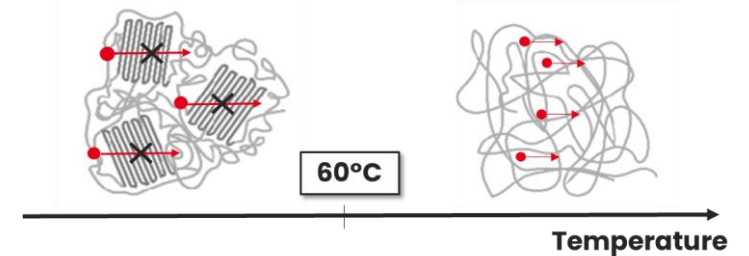
► Li/Polymer Matrix Interactions

- High coordination of Li⁺ ions
- Transference number $\approx 0.2 - 0.3$



► Semi-crystalline Polymer

- **Non-conductive** crystalline phases
- Conductivity **drops at rt.**



► Electrochemical Stability

- Stability up to **4V vs. Li⁺/Li₀**
- Limited to **low voltage cathode materials**



Polymer electrolytes: PEO

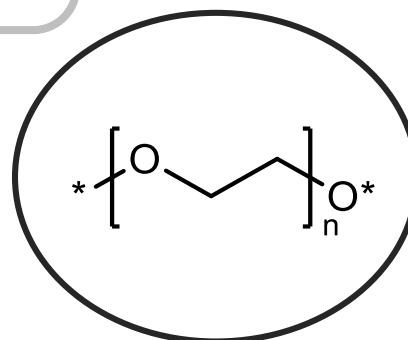
► Li⁺ Conductivities

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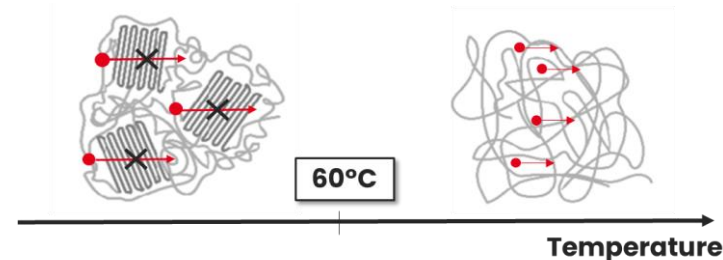
► Li/Polymer Matrix Interactions

- High coordination of Li⁺ ions
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► Semi-crystalline Polymer

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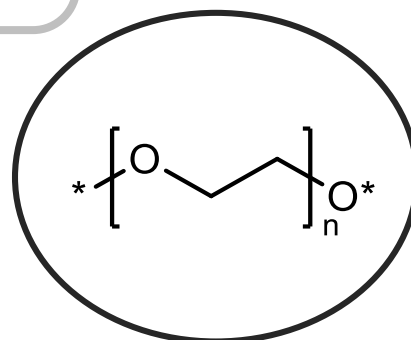


Study of other polymer families : polycarbonates

Polymer electrolytes: PEO

▶ Li⁺ Conductivities

- Ionic conductivity about 1 mS.cm⁻¹ at 80°C
- Low glass-transition temperature (T_g = -60°C)



▶ Li/Polymer Matrix Interactions

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▶ Semi-crystalline Polymer

- Non-conductive crystalline phases
- Conductivity drops at rt.



▶ Electrochemical Stability

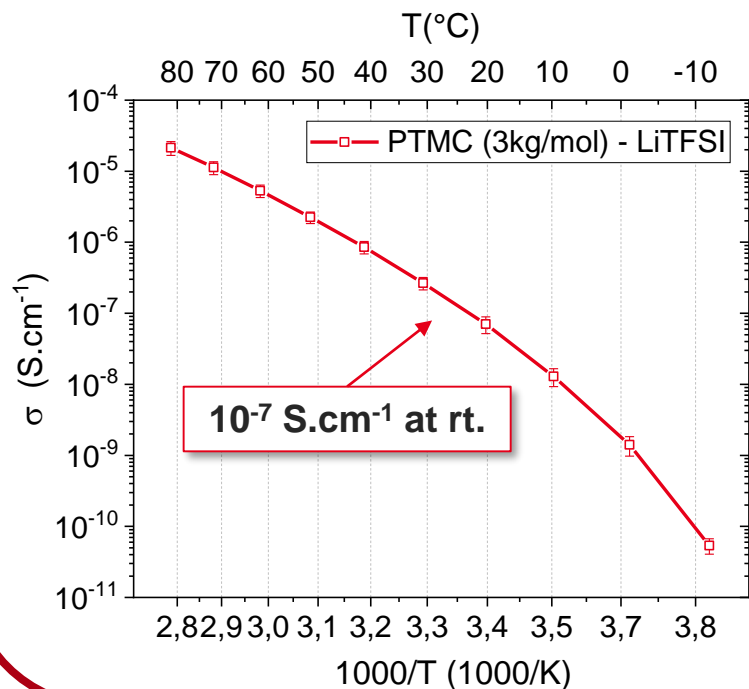
- Stability up to 4V vs. Li⁺/Li₀
- Limited to low voltage cathode materials



Single-ion approach

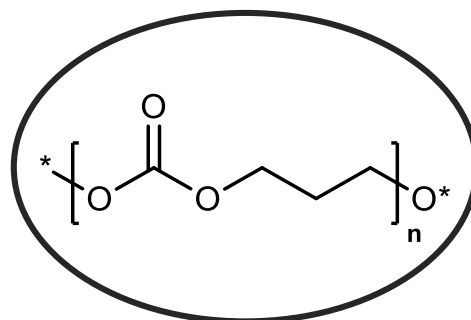
Polymer electrolytes: PTMC

▶ Li⁺ Conductivities



▶ Li/Polymer Matrix Interactions

- Low coordination of Li⁺ ions
- Transference number = 0.7 – 0.8 [1]

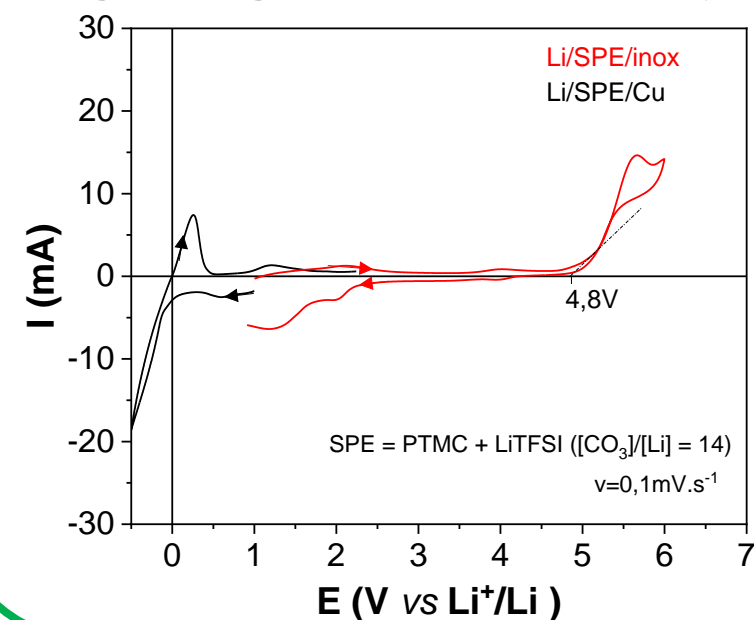


▶ Amorphous Polymer

- Low glass-transition temperature ($T_g = -20^\circ\text{C}$)

▶ Electrochemical Stability [2]

- Stability up to 4.8V vs. Li⁺/Li₀
- High voltage cathodes compatibility (NMC)

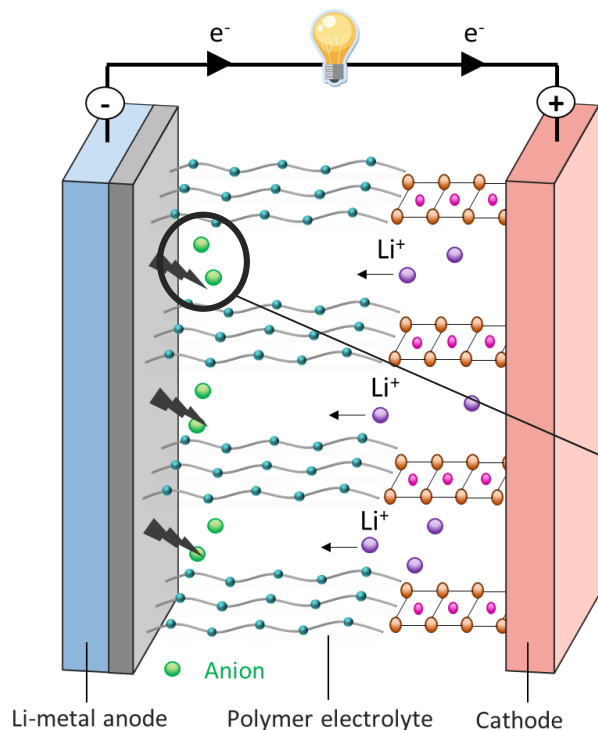


[1] B. Sun, J. Mindemark, E.V. Morozov, L. T. Costa, M. Bergman, P. Johansson, Y. Fang, I. Fűrób, D. Brandell, *Phys. Chem. Chem. Phys.* **2016**, 18, 9504–9513.

[2] T. Clement (2021). [Doctoral thesis, Univ. Grenoble Alpes]

Single-ion polymer electrolytes (SIPE)

Classic polymer electrolyte

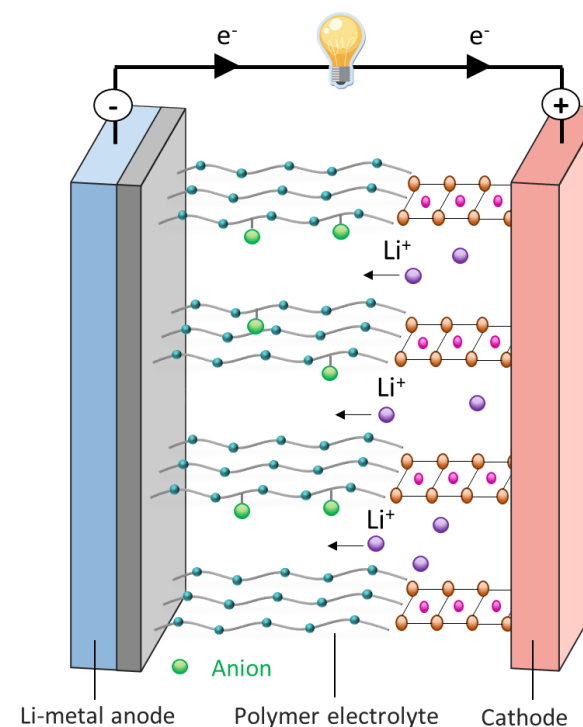


Covalent grafting of anions on polymer chains

Charge accumulation



Single-ion polymer electrolyte



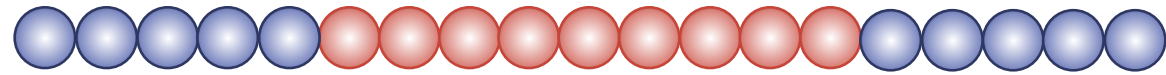
Dendritic growth due to cell polarization



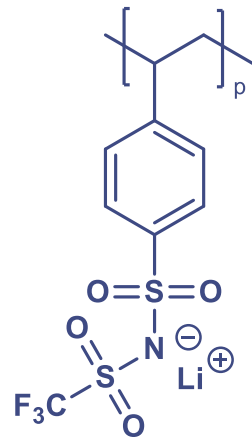
Only Li⁺ ions move via the segmental motion of polymer chains ($t_{Li^+} \approx 1$)

Single-ion polymer electrolytes (SIPE)

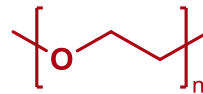
► Literature [1]:



Non-conductive
single-ion block

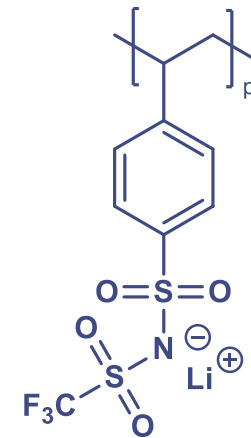


Conductive block



PEO

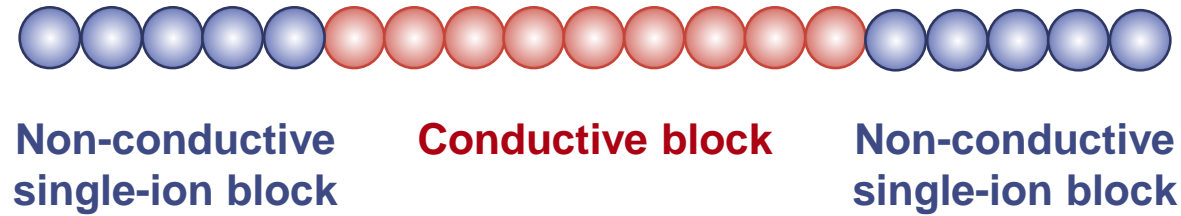
Non-conductive
single-ion block



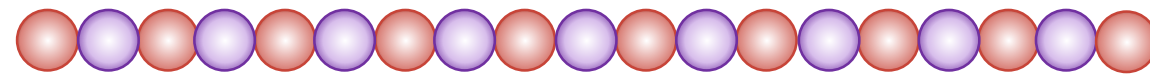
Phase
separation

Single-ion polymer electrolytes (SIPE)

► Literature [1]:

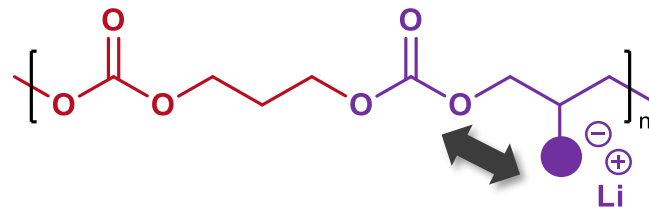


► Our work objectives:



**New SIPE
Architecture**

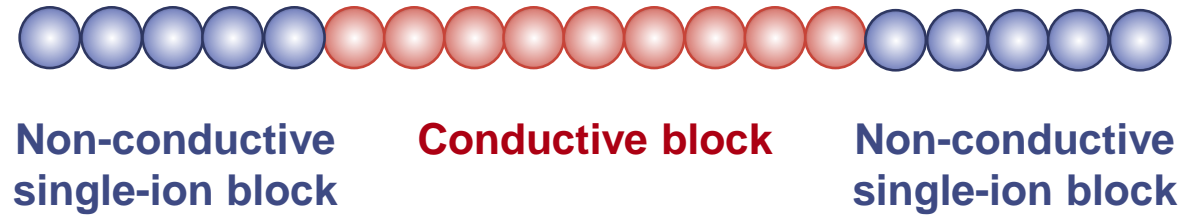
- Conductive moiety
- Single-ion and conductive moiety



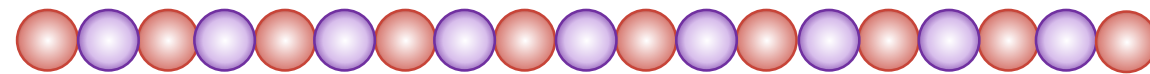
✔ Close proximity of **single-ion** and **conductive moieties**

Single-ion polymer electrolytes (SIPE)

► Literature [1]:

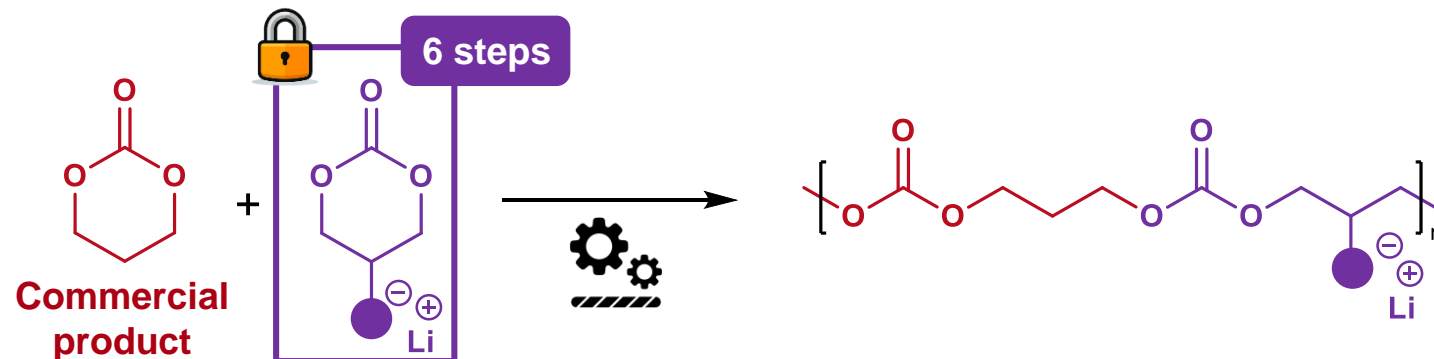


► Our work objectives:



New SIPE Architecture

- Conductive moiety
- Single-ion and conductive moiety

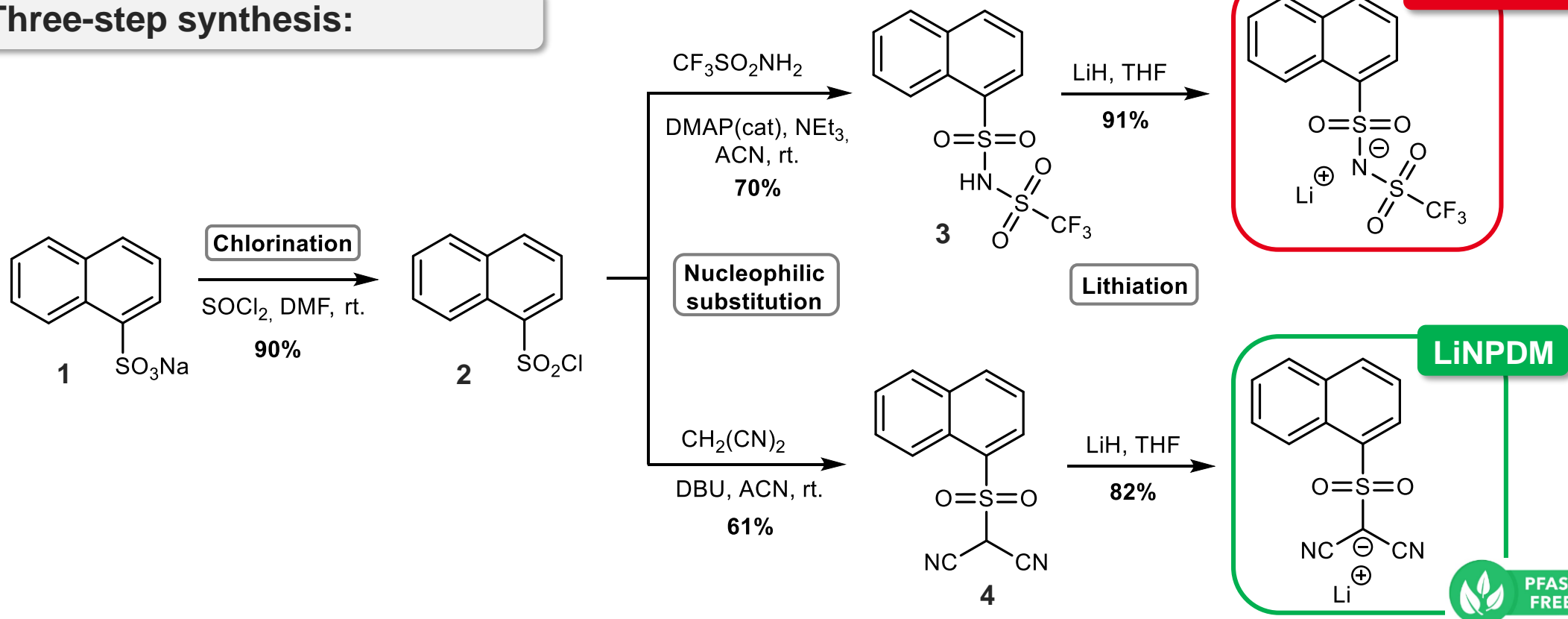


Naphthalene-derived model lithium salts

Study objectives

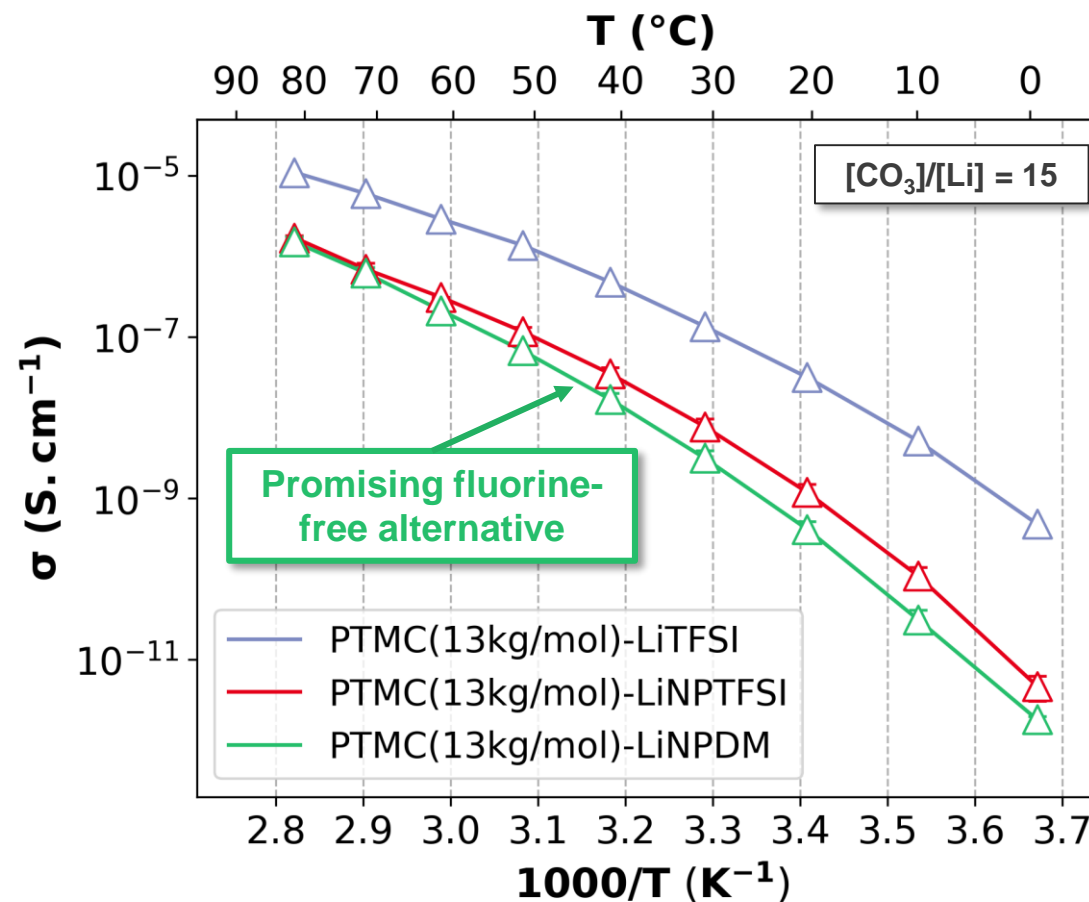
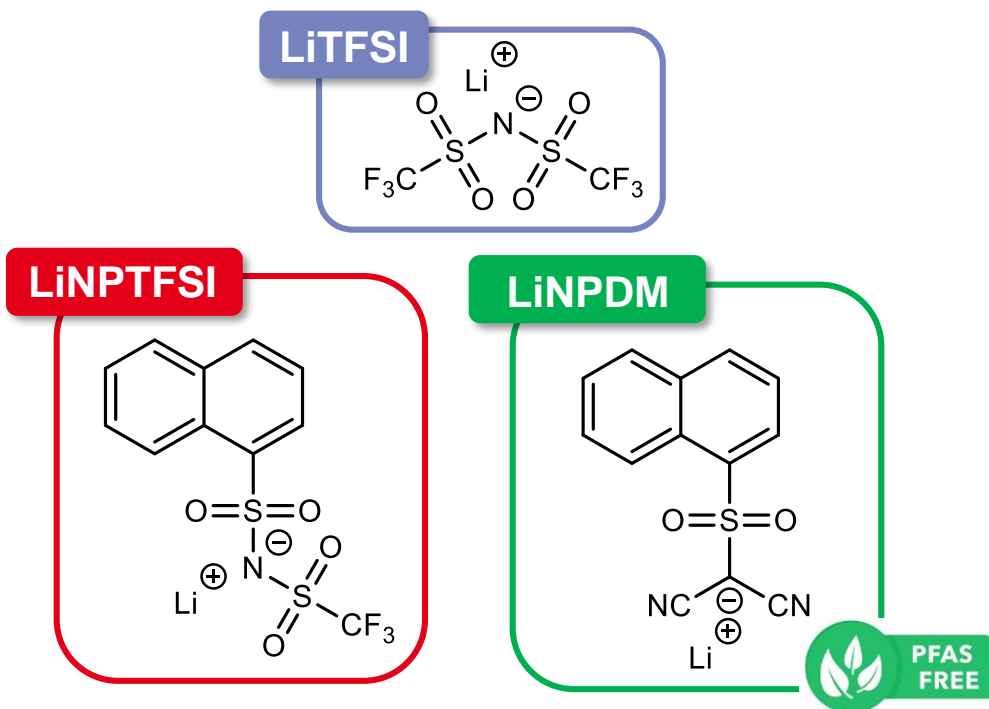
- Identify and **overcome synthesis bottlenecks** for a simple molecule
- Conduct a preliminary **electrochemical study**

Three-step synthesis:



Naphthalene-derived model lithium salts

Electrochemical characterizations:



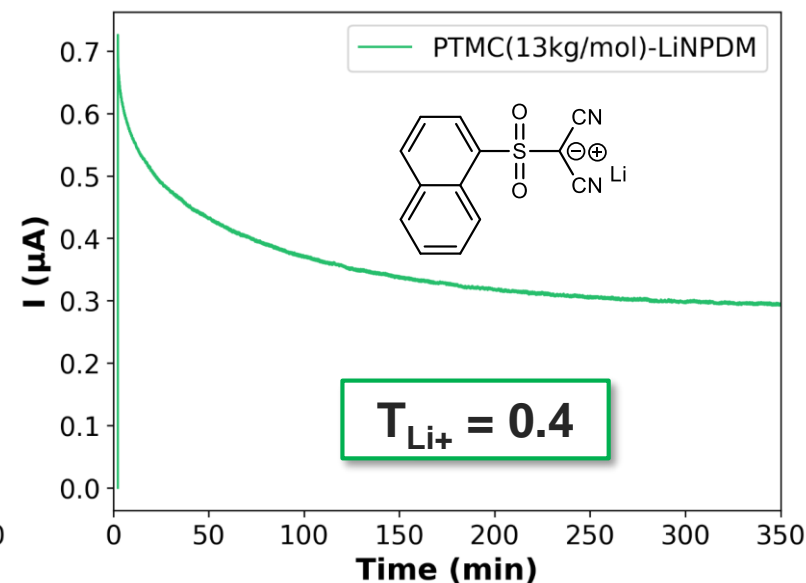
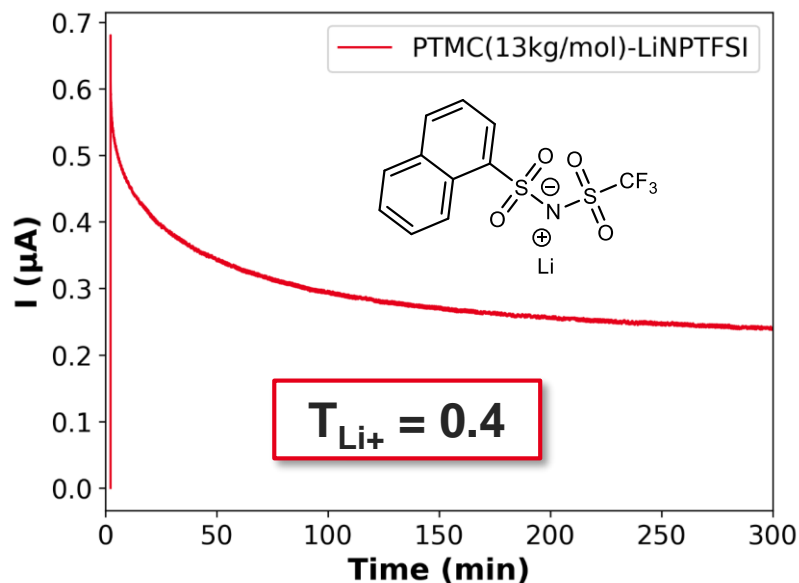
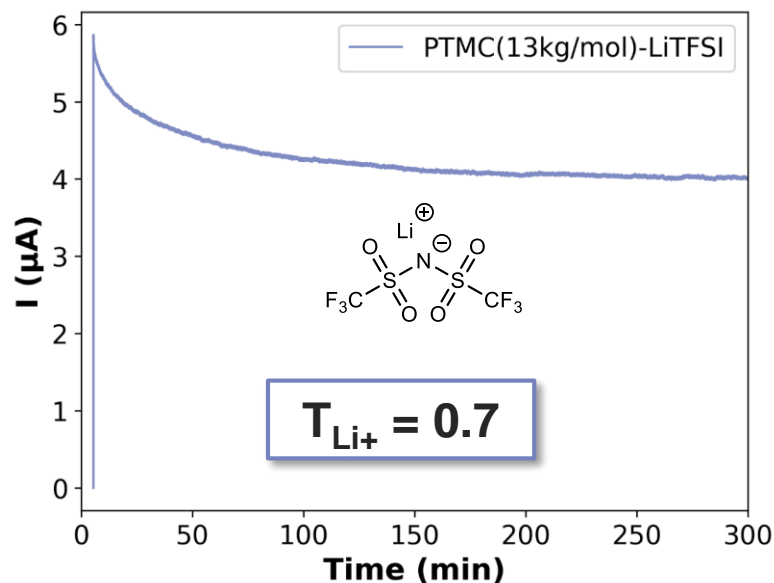
□ Hypothesis : Ionic conductivity is more influenced by **anion flexibility** than by **charge delocalization** [1]

Naphthalene-derived model lithium salts

Electrochemical characterizations:

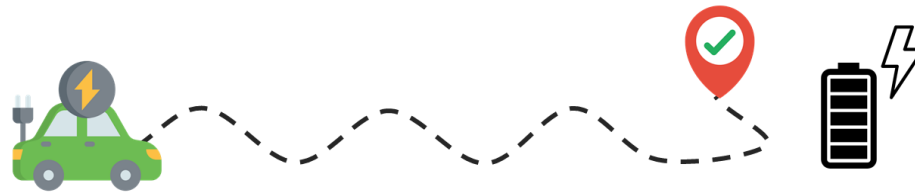
$$\text{Bruce-Vincent method: } T_{\text{Li}^+} = \frac{I_{\text{SS}}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{\text{SS}} R_{\text{SS}})}$$

$$\Delta V = 20 \text{ mV}, T = 60^\circ\text{C}$$



- ❑ Mobility of naphthalene-based anions is higher than TFSI
- ❑ Hypothesis : Naphthalene group is less bulky than $-\text{CF}_3$ group

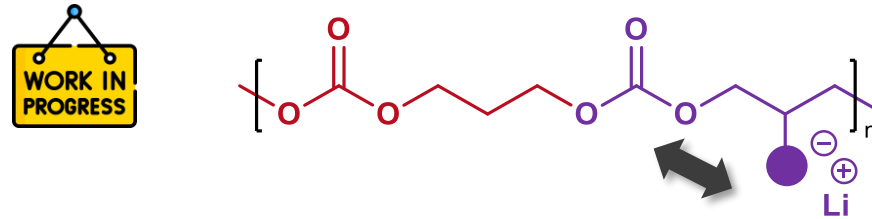
Conclusions



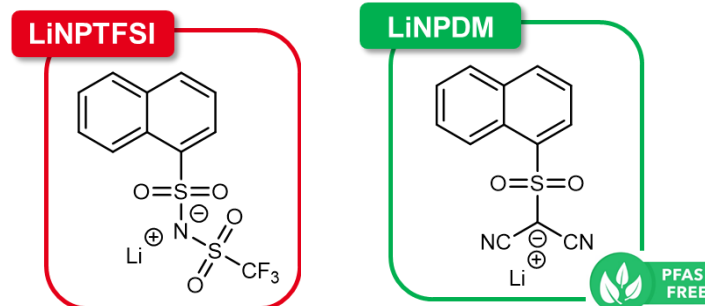
❑ Polycarbonates are an alternative to PEO for high-energy-density batteries

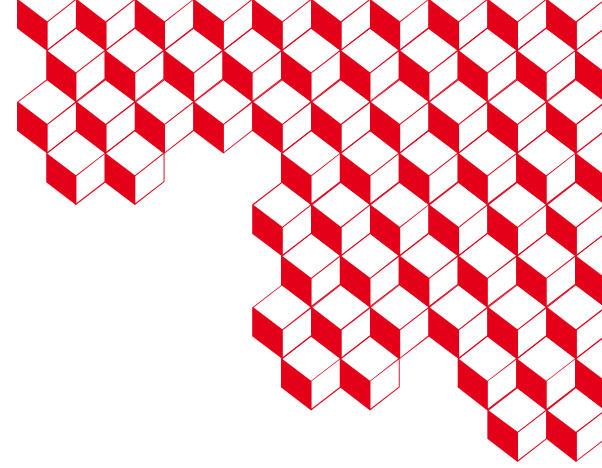
- Amorphous polymer
- Electrochemical stabilities up 4.8V vs. Li^+/Li_0
- High transference number ($T_+ = 0.7 - 0.8$)

❑ Development of an innovative carbonate-based SIPE architecture



❑ Electrochemical characterizations of original naphthalene-based lithium salts in polymer electrolyte systems





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Thank you for
your attention

Many thanks to my supervisors:

- Dr. Laurent Bernard
- Dr. Nicolas Leconte
- Dr. Matthieu Landa
- Dr. Lionel Picard



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DÉFENSE**

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