

Crosslinked Single-ion Conductor Polymer Electrolytes

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A05-0981

1- Introduction

- Synthesis and compositions

2- Transport Properties

“Grain boundaries”, “Bulk contributions”
and lithium interfaces

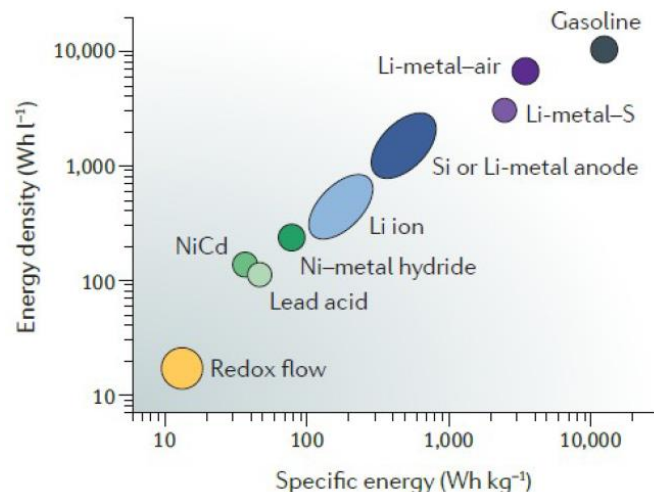
- Ionic conductivity σ (S.cm⁻¹)
 - Electrochemical impedance spectroscopy
 - Model Vogel-Tamman-Fulcher (VTF)
- Transference number t^+
- Ambipolar diffusion coefficient D_{amb} (cm².s⁻¹)

3- Stability

- Electrochemical Stability Window

- Context**

Need to develop high energy density and safe batteries [1]



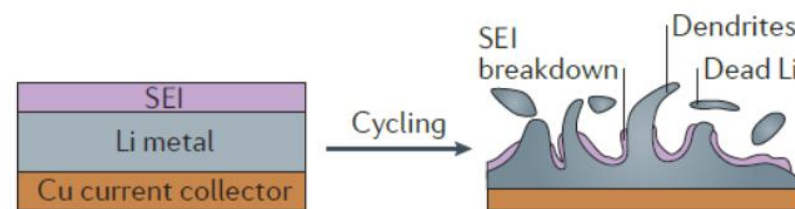
- Perspective**

Reliable battery with a negative electrode in Li metal

- Issue**

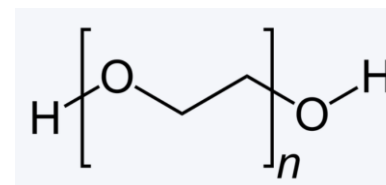
Li metal with conventional liquid electrolytes

→ Short-circuit hazard: flammable electrolyte and dendritic growth [1]

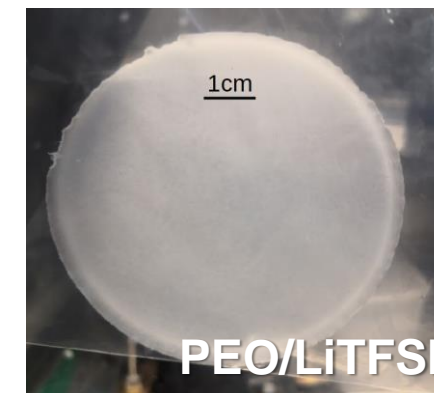


- Solution** [2]

Replace liquid electrolytes with **Solid Polymer Electrolytes (SPE)**



PEO :
Poly(ethylene oxide)



[1] : J.Lopez *et al.*, *Nature Reviews Materials* volume 4, 312–330 (2019)

[2] : M.Armand. *Solid State Ionics* 69, 309-319 (1994)

Interests

- Single-ion:

High transference number

$$t^+ = 0.85 - 0.95 \text{ [1]}$$

Great interest in preventing dendrite growth and addressing the limited power delivery [2]

- Crosslinked:

Increase the mechanical properties

- Silica network:

Simple and innovative one-step chemistry

Synthesis of the electrolytes

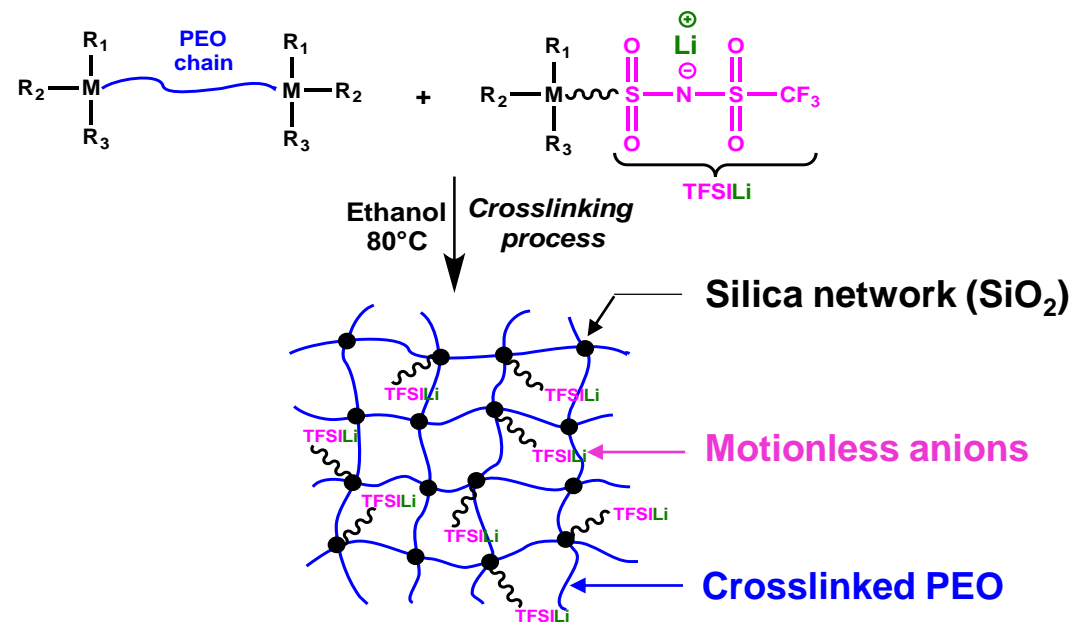


Table of the different compositions

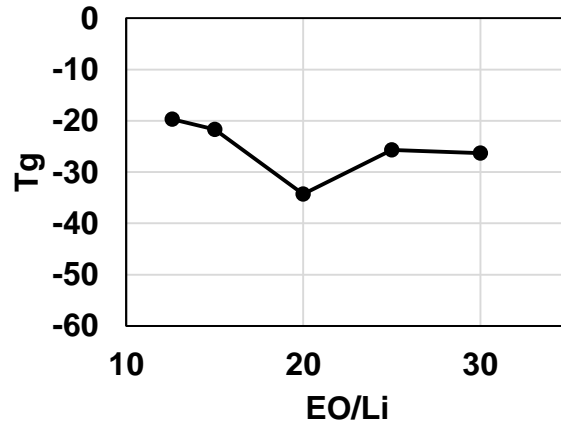
Samples	SI_13	SI_15	SI_20	SI_25	SI_30
EO/Li	12.6	15	20	25	30
Ethyl-TFSILi (wt%)	29.3	26	21	17.6	15.2

[1] : Devaux *et al. Electrochim. Acta.*, 269, 250-261 (2018)

[2] : Chazalviel, J-N. *Phys. Rev. A* 42, 7355–7367 (1990)

- **DSC**

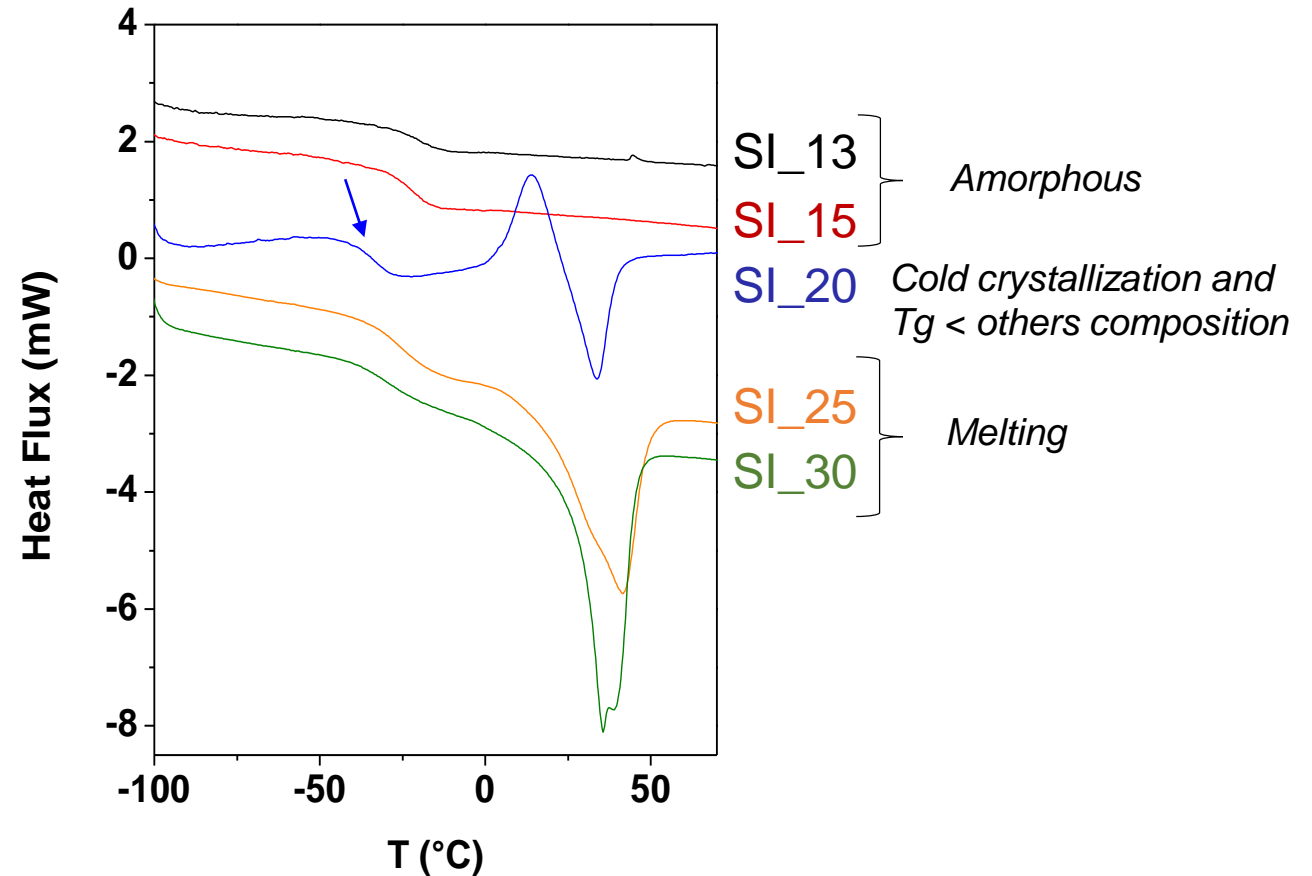
- Heating scan from -110 to 130 °C at 20 °C/min
- T_g determined as the pic of the derivative curve



Samples	SI_13	SI_15	SI_20	SI_25	SI_30
EO/Li	12.6	15	20	25	30
T_g (°C)	-20	-22	-34	-26	-26

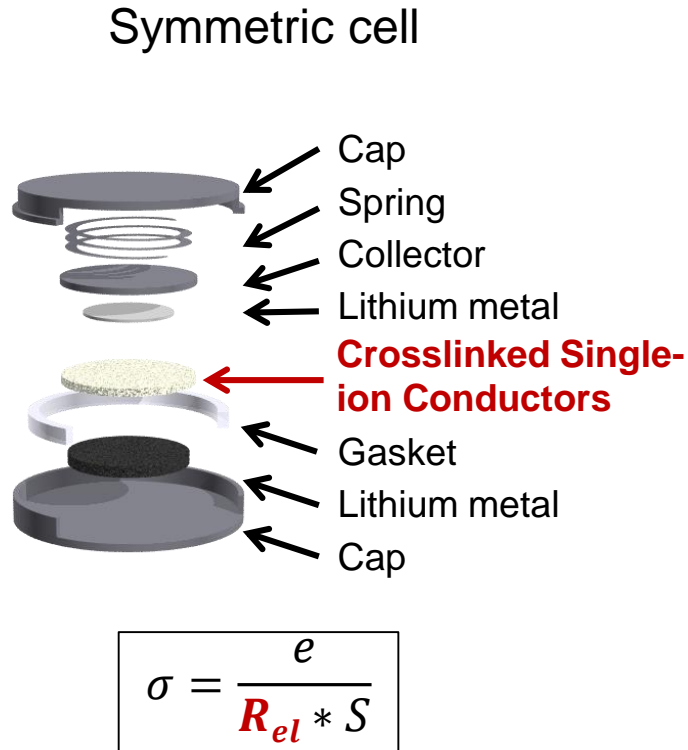
- T_g presents a minimum at EO/Li = SI_20
- Behavior different from PEO/LiTFSI.^[1]

- **Melting thermograms**



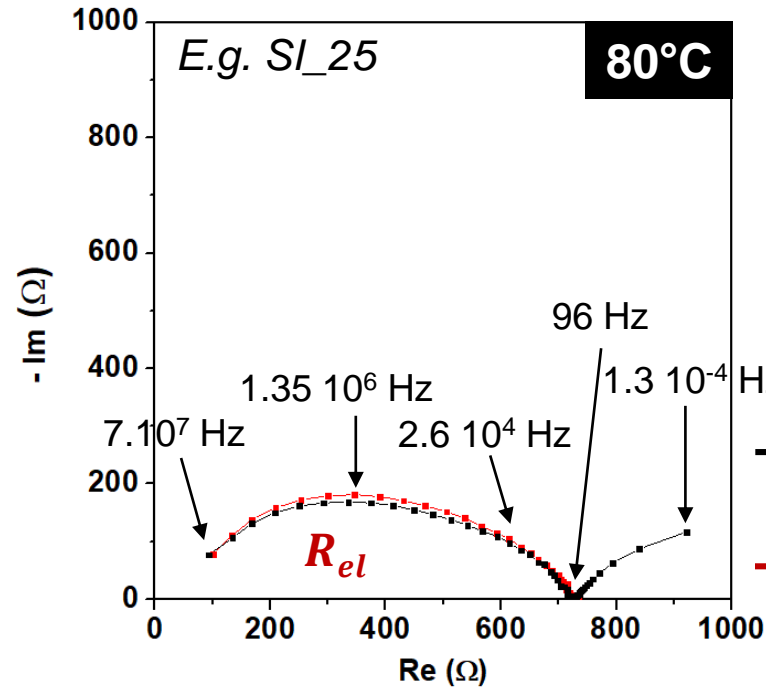
[1] S. Lascaud *et al.* *Macromol.* 27, 7469-7477 (1994)

- Electrochemical Impedance Spectroscopy (EIS)**

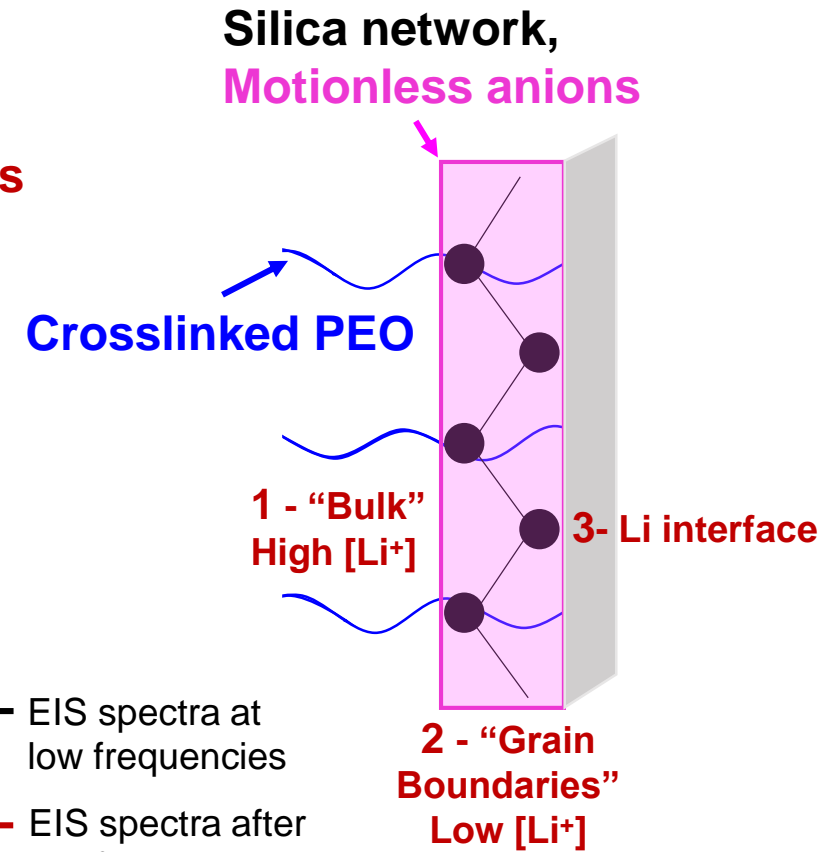


σ : Ionic Conductivity (S.cm⁻¹)
 R_{el} : Electrolyte resistance
 e : Thickness of the electrolyte
 S : Surface of the electrodes

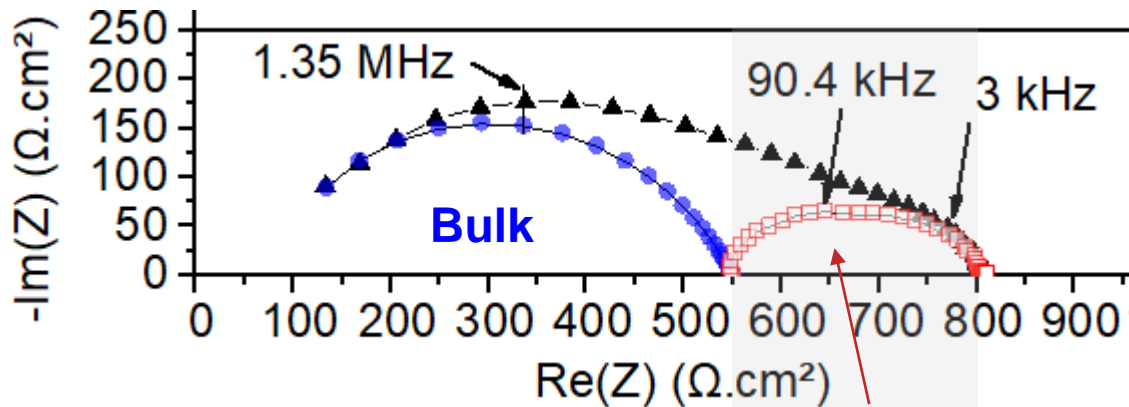
Crosslinked Single-ion Conductors



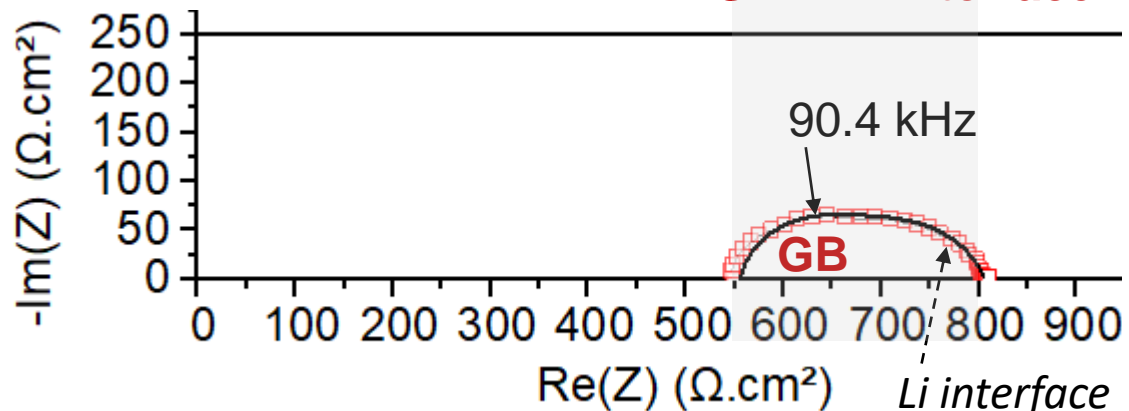
→ EIS Spectra: very distributed in frequencies with **3 main** contributions



➤ Li/SI/Li cell

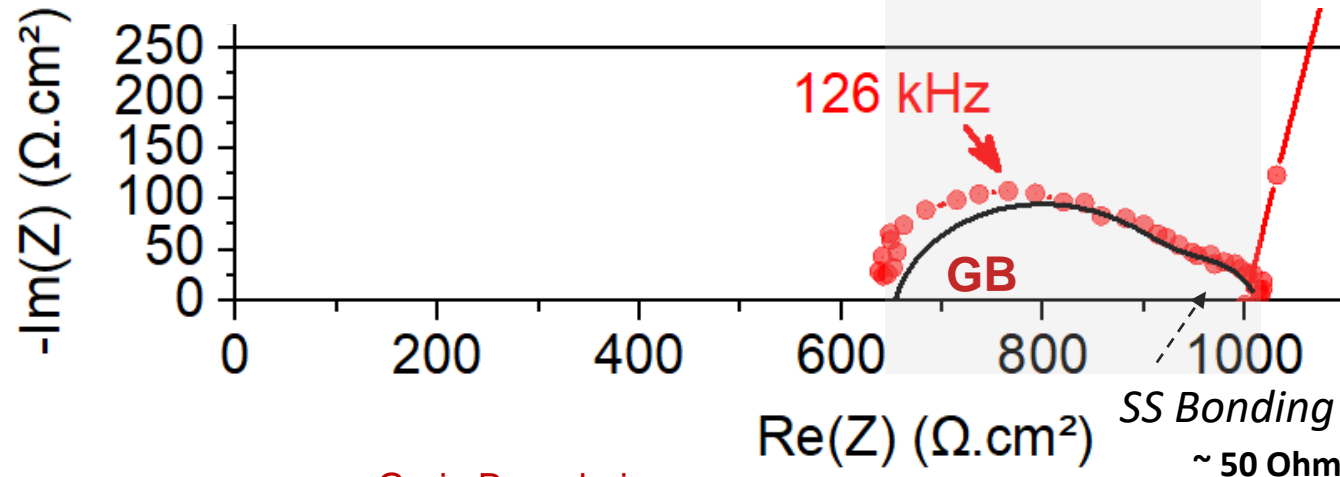
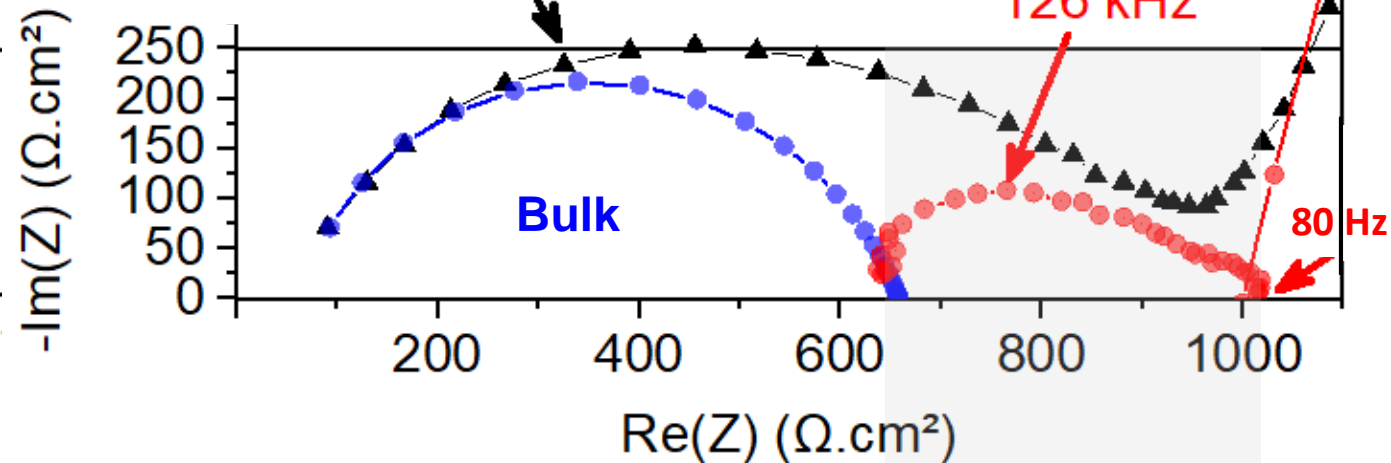


GB + Li interface



Li interface
~ 80 Ohm

➤ SS/SI/SS cell 1.31 MHz



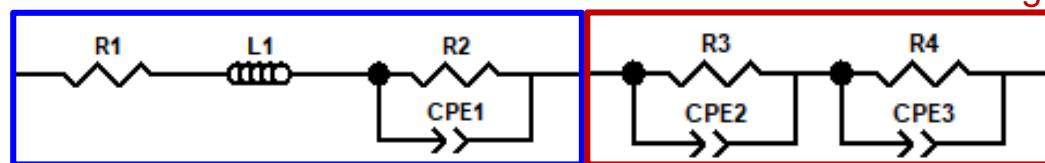
SS Bonding
~ 50 Ohm

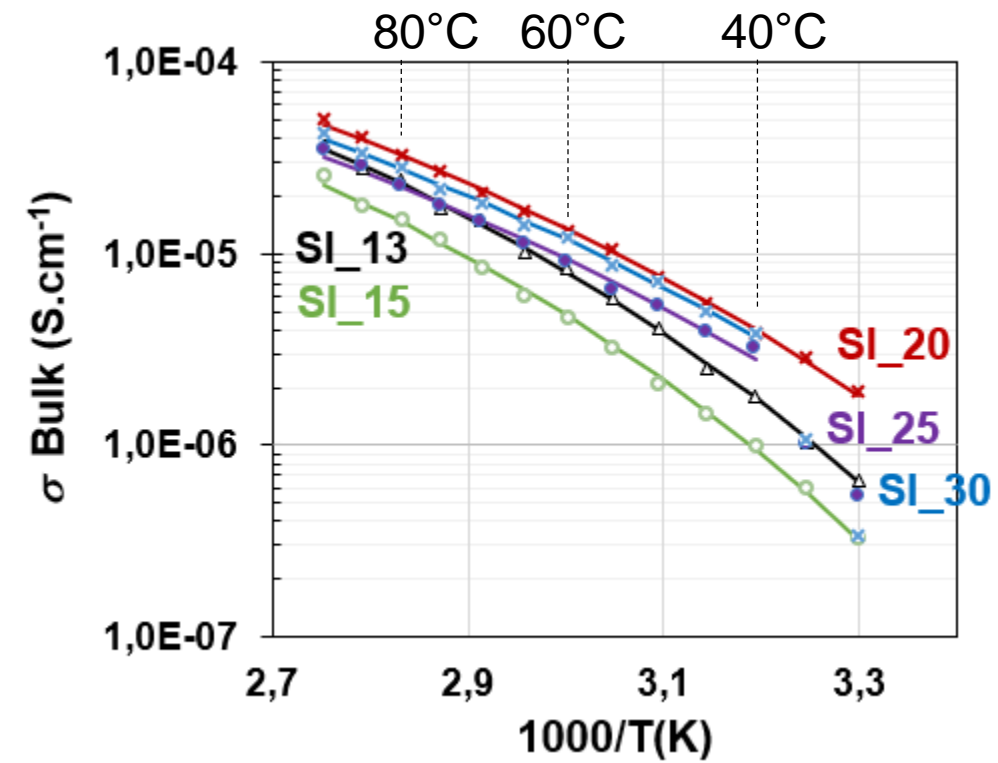
SI_15 at 80°C

- Frequencies are similar
- SS and Li values of the **GB** & **Bulk** are identical
- Very small **Li interface**

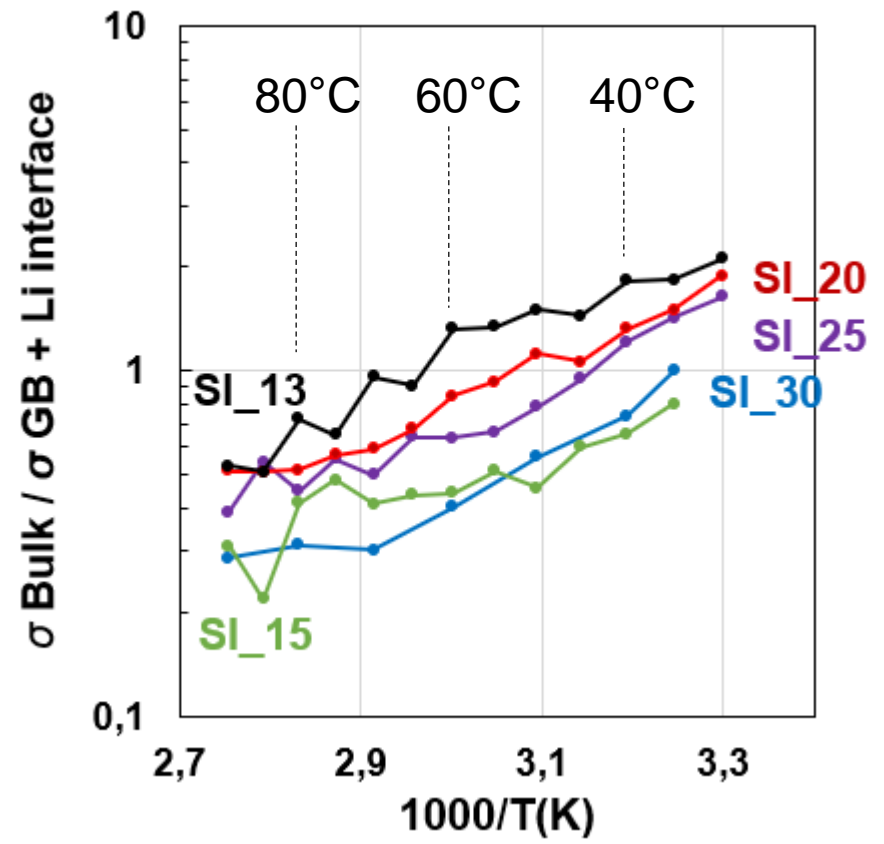
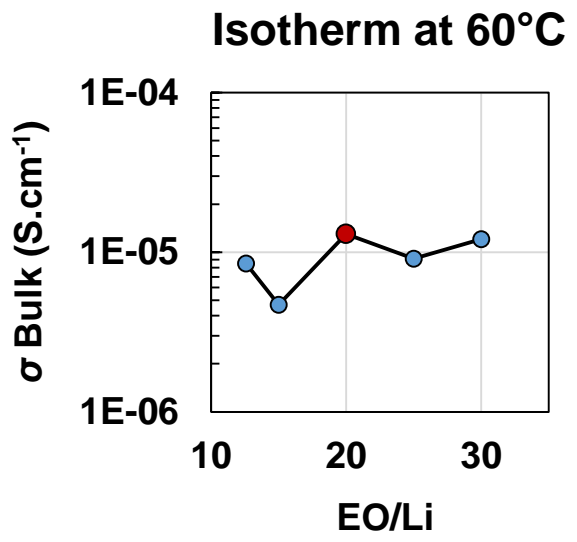
Cables + Bulk

Grain Boundaries +
Interface Li or SS Bonding



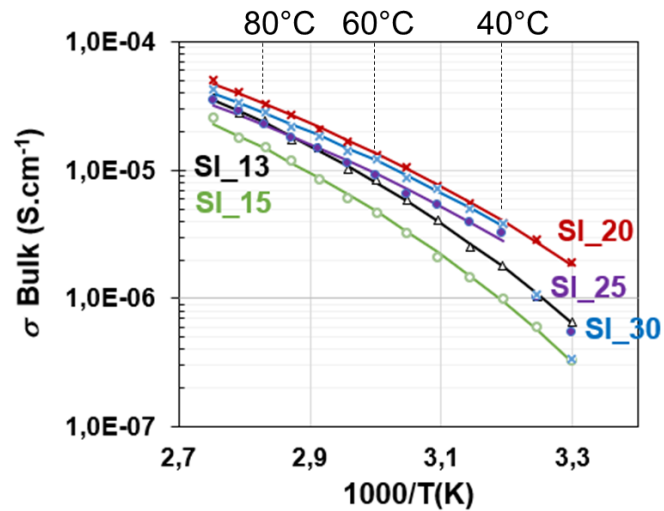


Ionic conductivity σ_{Bulk} max for **SI_20**



$\sigma_{\text{Grain Boundaries}} / \sigma_{\text{Li interface}}$ shows similar curves

→ Similar behavior between compositions



$$\sigma = \frac{A}{T^{1/2}} e^{-\frac{B}{T-T_0}} \text{ (VTF)}$$

σ : Ionic conductivity (S.cm⁻¹)

T : Temperature (K)

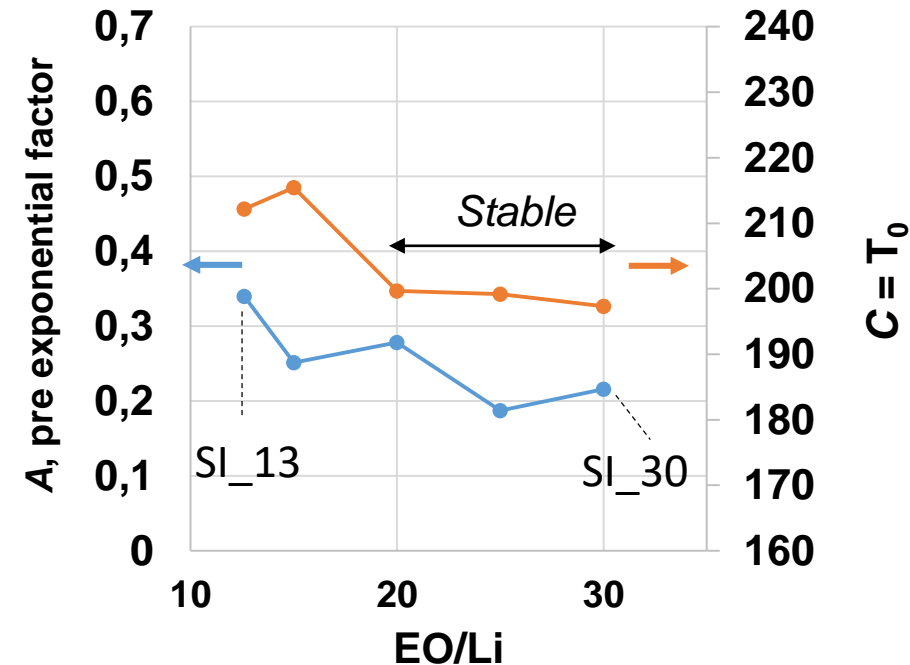
A : Pre exponential factor

B : Pseudo energy of activation

$T_0 = T_g - 50$, T_g glass transition temperature

Samples	SI_13	SI_15	SI_20	SI_25	SI_30
EO/Li	12.6	15	20	25	30

Conditions : σ Bulk, B ($E_a = 7.8$ kJ/mol)



→ A and T_0 are consistent with the literature [1]

[1] : Devaux *et al. Electrochim. Acta.*, 269, 250-261 (2018)

- Diffusional impedance at low frequencies ($10 - 10^{-4}$) Hz [1-2]

$$t^+ = \frac{\mu^+}{\mu^- + \mu^+} = \frac{R_e}{R_e + Rd}$$

μ^+, μ^- Mobility of the ions

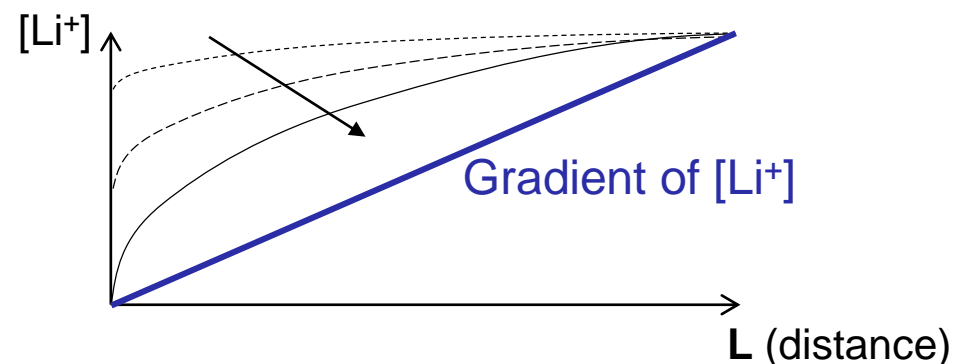
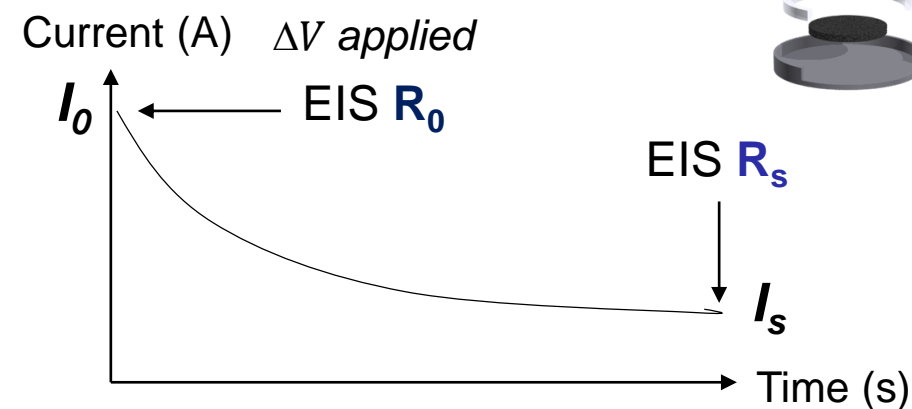
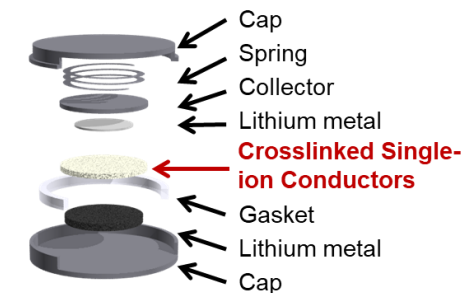
Rd Diffusional impedance (Warburg element)

- Impedance and potentiostatic polarization ΔV [3]

$$t^+ = \frac{R_{bulk}}{\frac{\Delta V}{I_s} - R_s}$$

R_{bulk} Bulk resistance

R_s Interface resistance



[1] : Bouchet *et al. J. Electroch. Soc.*, 150, A1385-A1389 (2003)

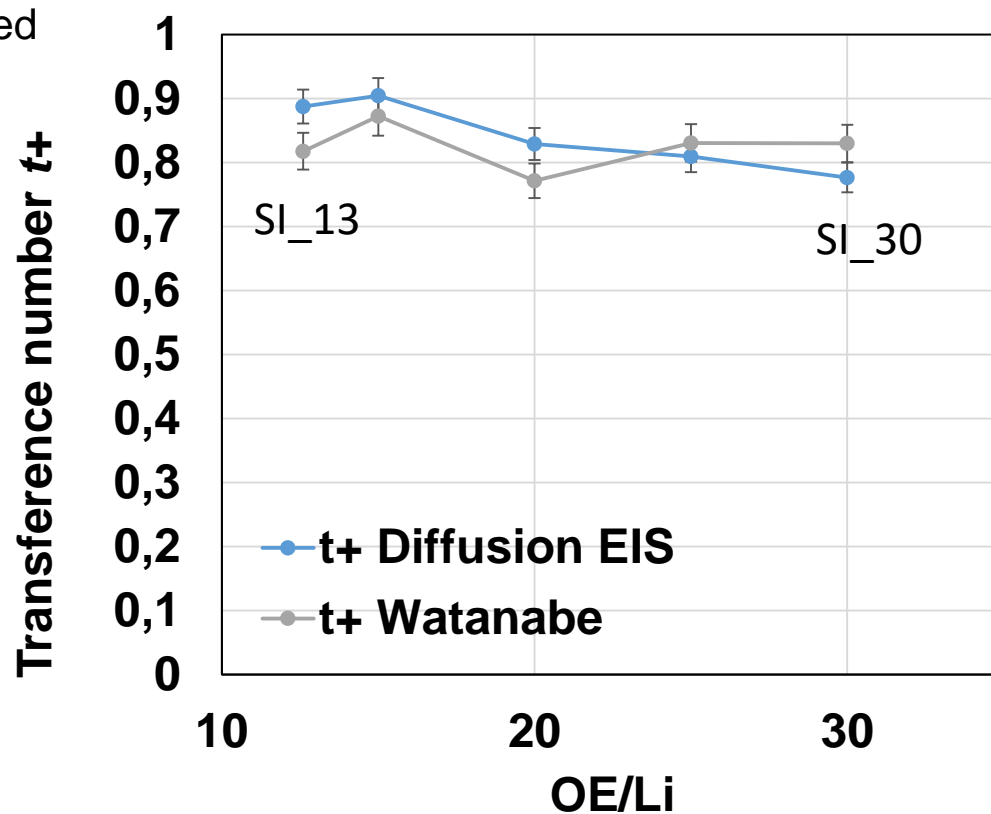
[2] : P. R. Sorensen, T. Jacobsen. *Electrochim. Acta.*, 27, 1671-1675 (1982)

[3] : M. Watanabe *et al. Solid State Ionics*, 28-30, 911-917 (1988)

Parameters:

- $T = 80^\circ\text{C}$
- EIS Amplitude: $\Delta E = 30 \text{ mV}$
- ChronoAmperometry applied
 $E = 80 \text{ mV}$

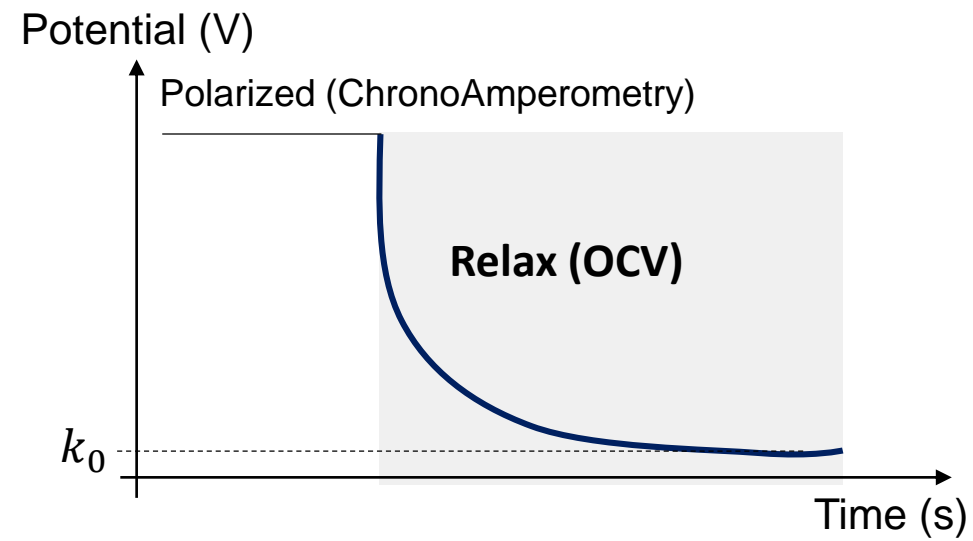
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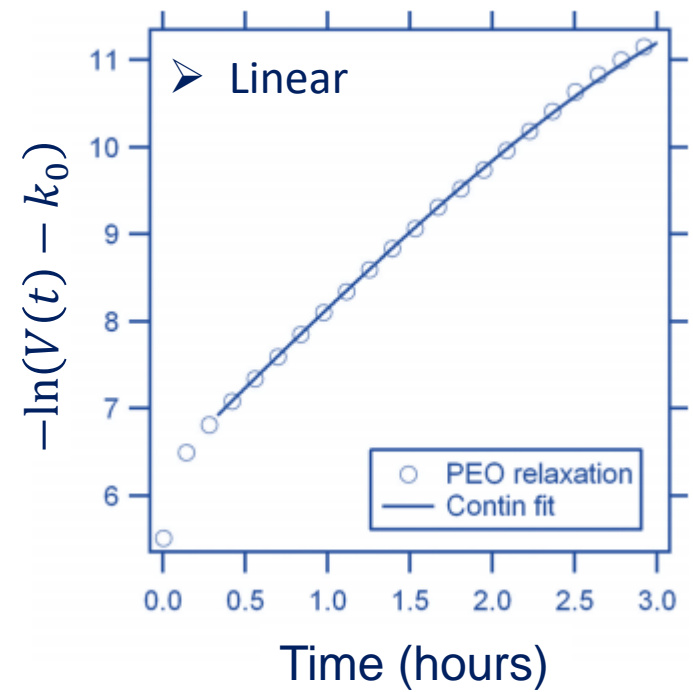
- t^+ is about 0.8 – 0.9
- not equal to 1 because of the interface reactions with the SPE [1]

[1] : Devaux *et al. Electrochim. Acta.*, 269, 250-261 (2018)

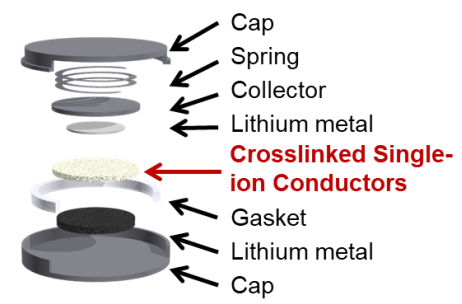
- Polarization followed by a relaxation [1-2]



$$V(t) = k_0 + k_1 e^{-\Gamma t}$$



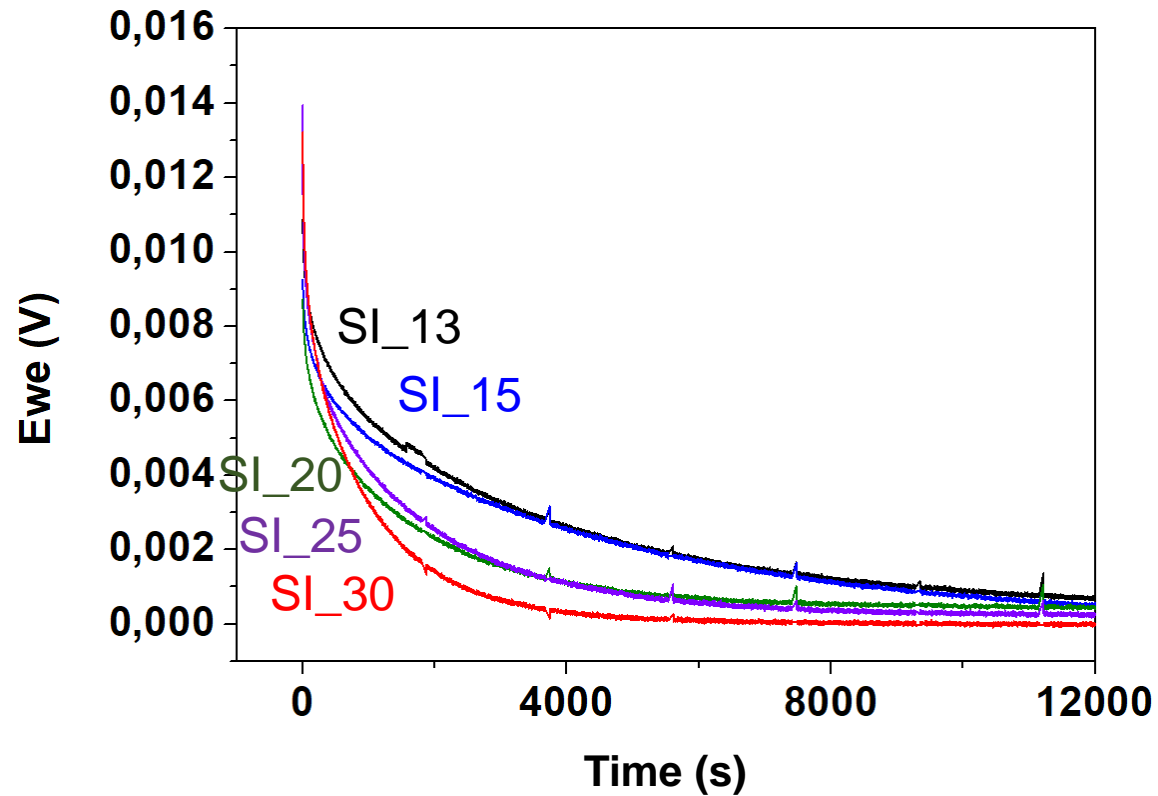
One mode of relaxation
(ex : PEO + LiTFSI)



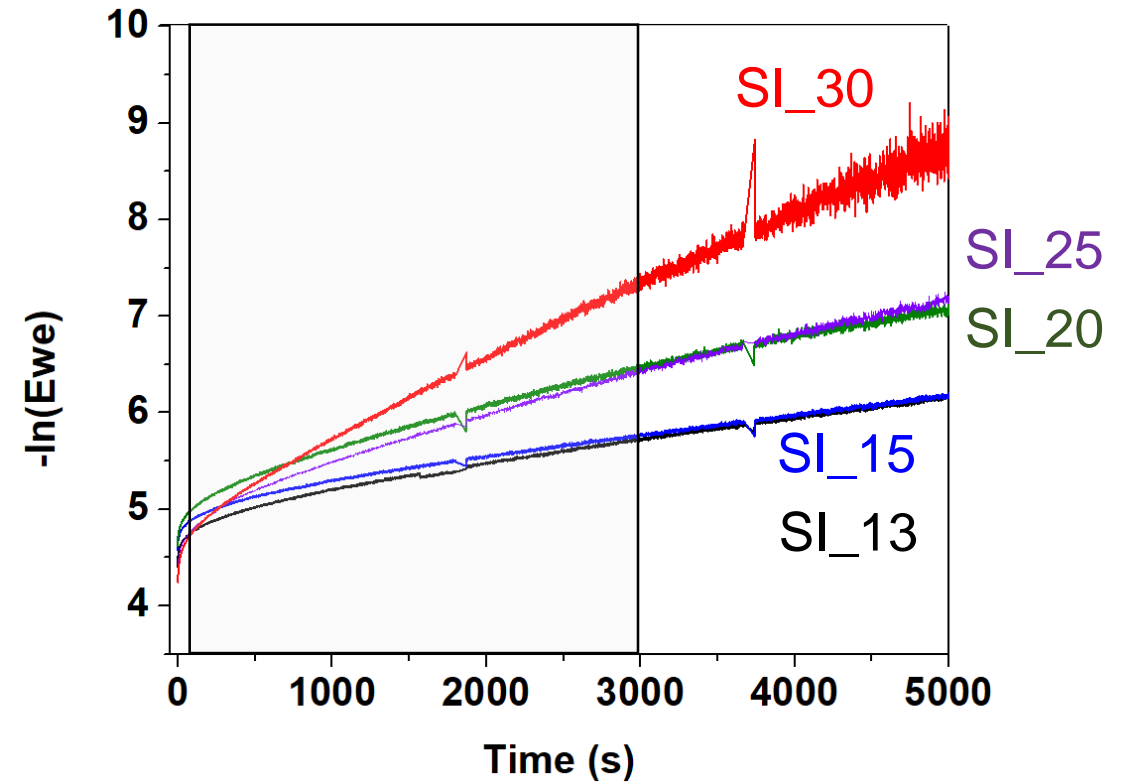
$$\text{with } \Gamma = D_{amb} \pi^2 / L^2$$

L : thickness of the electrolyte

[1] : S.D. Thompson and J. Newman, *J. Electrochem. Soc.*, 136, 3362 (1989)
 [2] : S. A. Mullin *et al.* *J. Electrochem. Soc.*, 158 A619 (2011)



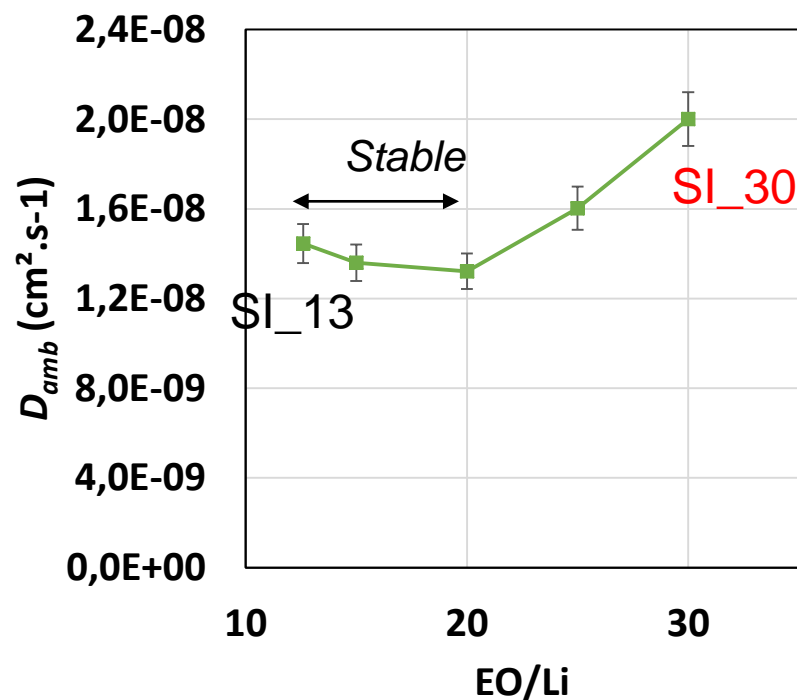
- Relaxation after polarization at 80°C



- Linear domain : up to ~ 3 000 s

$$V(t) = k_0 + k_1 e^{-\Gamma t}$$

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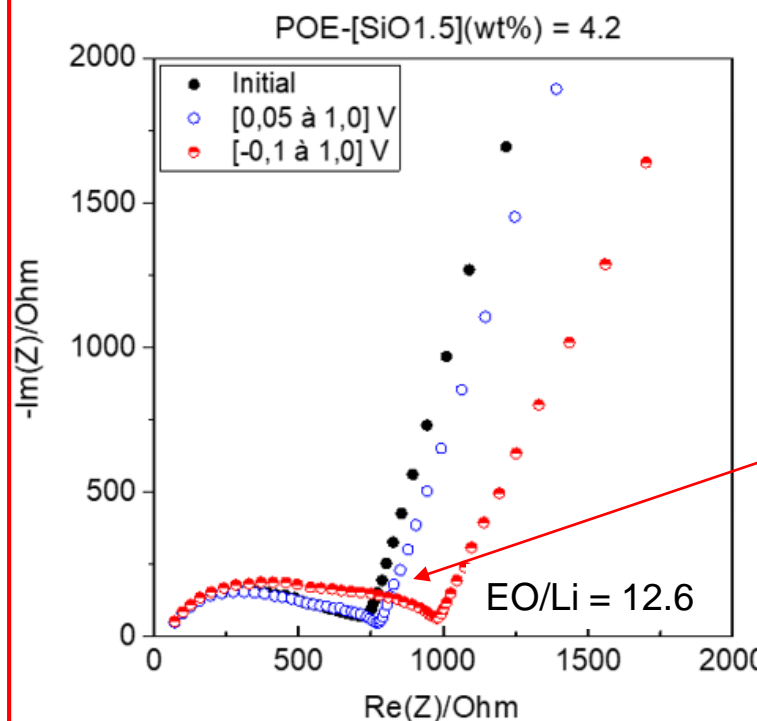
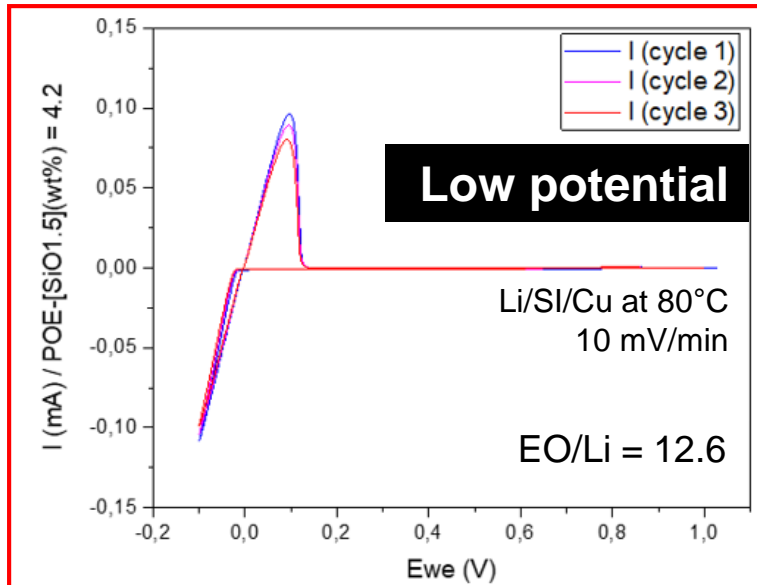
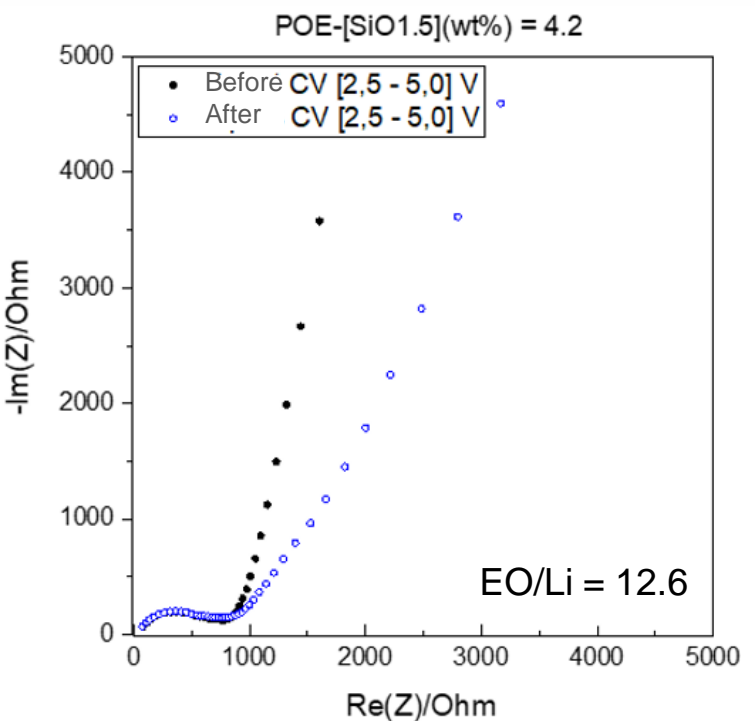
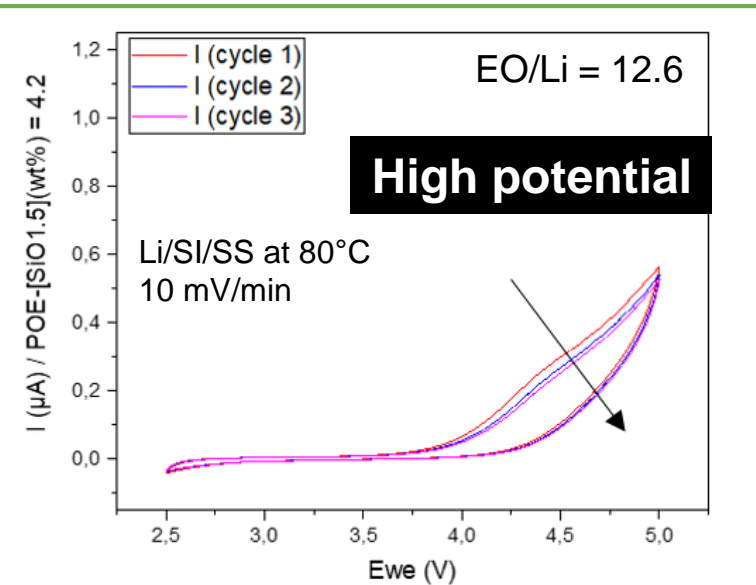


- EO/Li [13; 20] D_{amb} stable
- EO/Li [25; 30] D_{amb} increase

↓
Less crosslinked

- Values similar at a copolymer PEO-PS ($\sim 2 \times 10^{-8}$ cm².s⁻¹ [1])
→ D_{amb} is dependent on the chain dynamic

[1]: Scott A. Mullin *et al.* *J. Electrochem. Soc.*, 158 A619 (2011)



High potential scan up to 5V vs Li⁺/Li

- After 3.8 V the degradation of the electrolyte starts (μA) but I decreases

→ EIS spectra evolve slightly

Passivation

Li reduction & oxidation scan down to -0.1 V vs Li⁺/Li

- From -0.1 to 0.2 V current is about ± 0.1 mA

→ EIS spectra evolve

Li interface and Grain boundaries increase

Conclusions and Perspectives

- Crosslinked Single-ion Conductor Polymer Electrolytes**

Synthesis: simple and in one-step

Organosilicon Nanocharges – charge carrier vs. organic chains synthesis (PEO based)

Electrochemistry: similar to a “single-ion PEO” electrolyte

Thermodynamic, ionic transport, and electrochemical stability

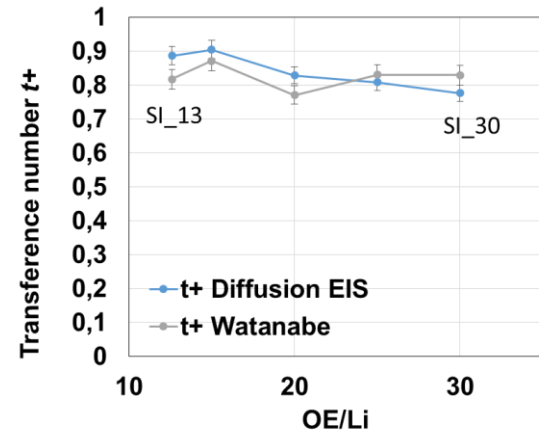
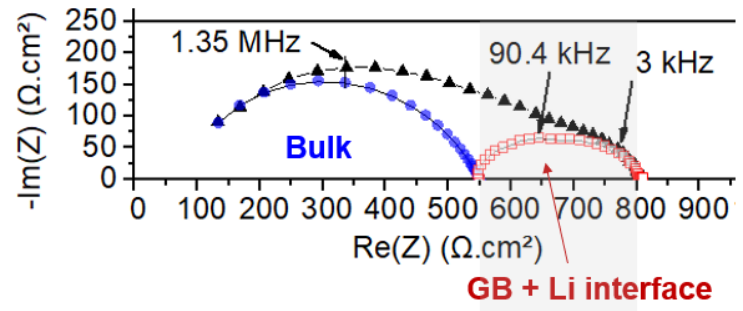
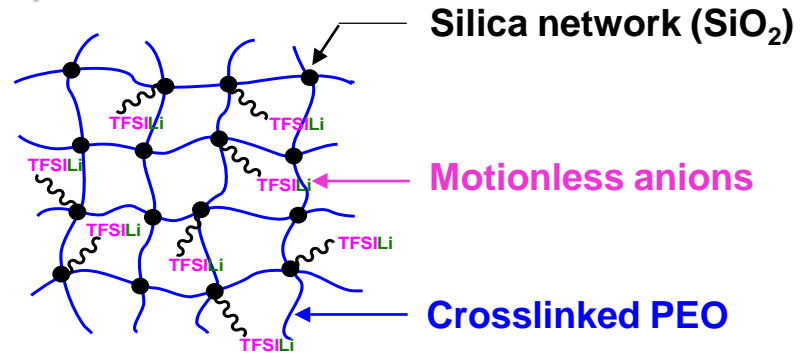
Difference: “Silica network & PEO”

In Impedance spectroscopy: 3 contributions “Bulk” “Grain Boundaries” and “Li interface”

- Perspectives**

Electrochemistry: Study of dendrite growth and battery tests

Material characterizations: SAXS measurements





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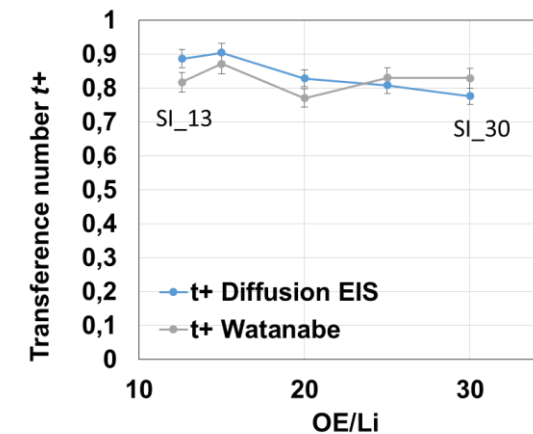
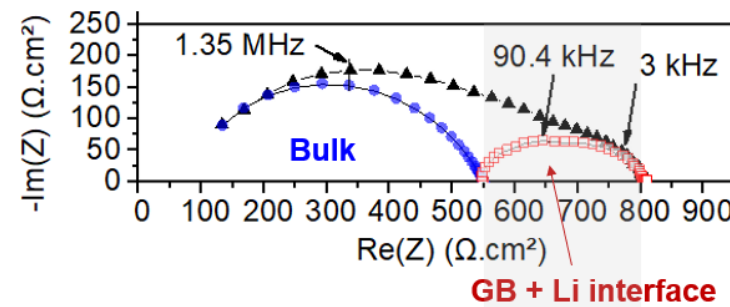
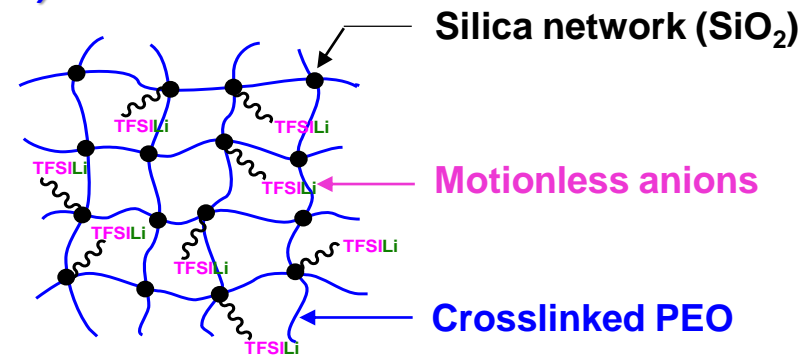
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Thank you for your attention!